Electron Transfer

Self-Sorting of Cyclic Peptide Homodimers into a Heterodimeric Assembly Featuring an Efficient Photoinduced Intramolecular Electron-Transfer Process

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Abstract: We describe the thermodynamic characterisation of the self-sorting process experienced by two homodimers assembled by hydrogen-bonding interactions through their cyclopeptide scaffolds and decorated with Zn–porphyrin and fullerene units into a heterodimeric assembly that contains one electron-donor (Zn–porphyrin) and one electron-acceptor group (fullerene). The fluorescence of the Zn–porphyrin unit is strongly quenched upon heterodimer formation. This phenomenon is demonstrated to be the result of an efficient photoinduced electron-transfer (PET) process occurring between the Zn–porphyrin and the fullerene units of the heterodimeric system. The recombination lifetime of the charge-separated state of the heterodimer complex is in the order of 180 ns. In solution, both homo- and heterodimers are present as a mixture of three regioisomers: two staggered and one eclipsed. At the concentration used for this study, the high stability constant determined for the heterodimer suggests that the eclipsed conformer is the main component in solution. The application of the bound-state scenario allowed us to calculate that the heterodimer exists mainly as the eclipsed regioisomer (75–90%). The attractive interaction that exists between the donor and acceptor chromophores in the heterodimeric assembly favours their arrangement in close contact. This is confirmed by the presence of charge-transfer bands centred at 720 nm in the absorption spectrum of the heterodimer. PET occurs in approximately 75% of the chromophores after excitation of both Zn–porphyrin and fullerene chromophores. Conversely, analogous systems, reported previously, decorated with extended tetrathiafulvalene and fullerene units showed a PET process in a significantly reduced extent (33%). We conclude that the strength (stability constant (*K*)×effective molarity (EM)) of the intramolecular interaction established between the two chromophores in the Zn–porphyrin/fullerene cyclopeptide-based heterodimers controls the regioisomeric distribution and regulates the high extent to which the PET process takes place in this system.

Introduction

In living organisms, molecular assemblies with tubular topology carry out remarkable tasks such as molecular recognition[1] or ion transport.[2] For this reason, they have inspired synthetic and supramolecular chemists.[3] In this vein and over the past two decades, the molecular self-assembly of cyclic peptides (CP) has been used for the construction of remarkable nanotubular structures.[4–7] The assembled nanotubular structures possess unique properties from which applications for the development of bio-inspired functional materials have been derived.[8–10] Owing to the ease of their synthesis and functional versatility, CP self-assembled architectures have been used in diverse areas of chemical research ranging from molecular recognition studies,[11,12] transmembrane transport[13,14] and investigation of antiamyloidogenic properties,[15] to charge transport in vertically aligned peptide nanotubes.[16]

The intermolecular, β-sheet-like hydrogen-bonding network that is established between C=O and N–H groups pertaining to the backbone amino acids of CP monomers constitutes the

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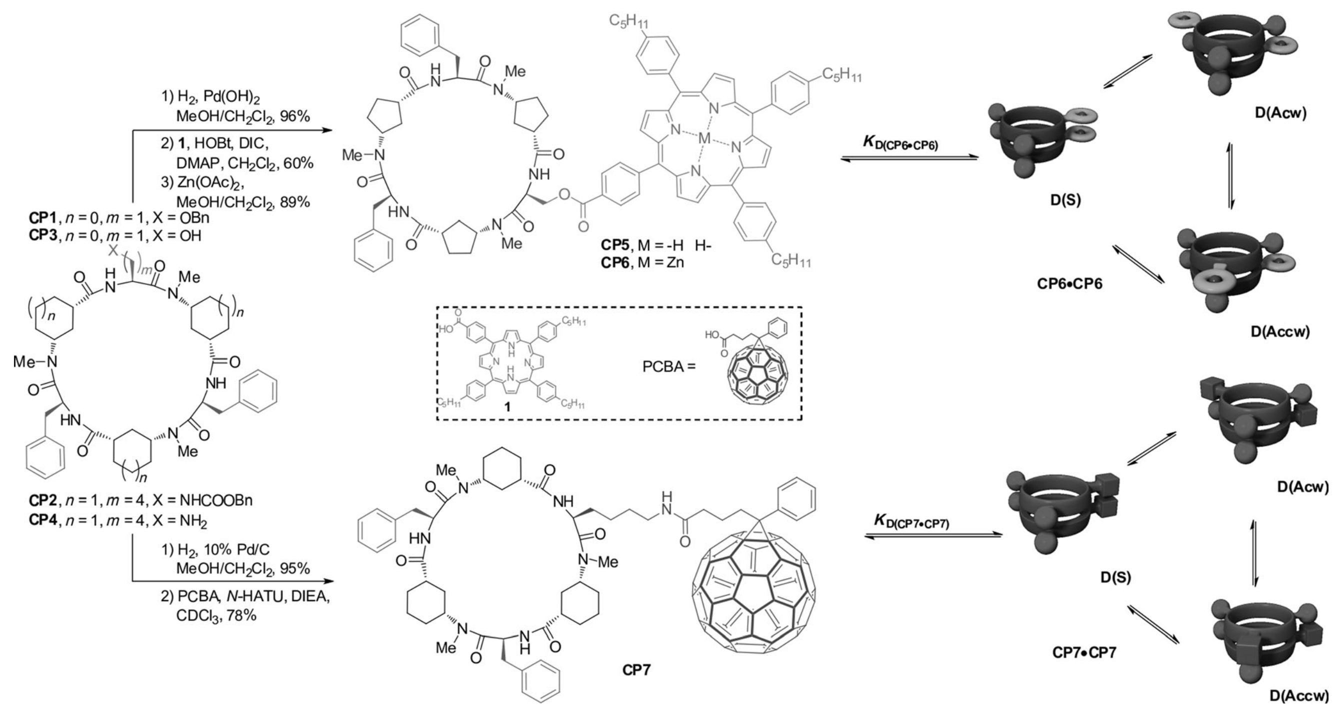
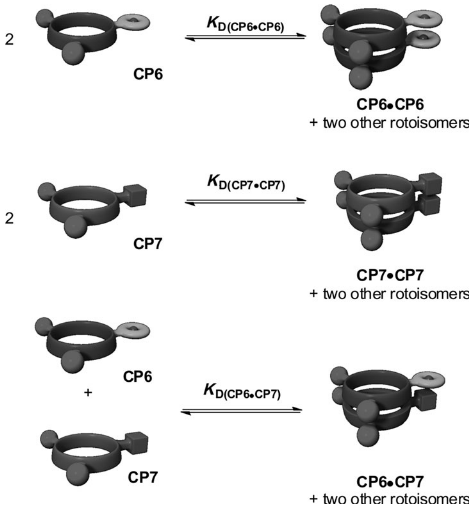


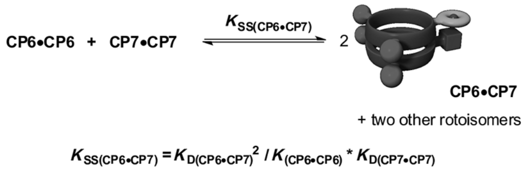
Scheme 1. Dimerisation process of cyclopeptides **CP6** (top) and **CP7** (bottom) (HOBt = 1-hydroxybenzotriazole, Bn = benzyl). The line-drawing structures of **CP6** and **CP7** are shown together with their schematic representation upon dimer formation. The three regioisomers of each dimer are represented as cartoon models.

essential driving force for the assembly of infinite supramolecular architectures with tubular topology. The desire to obtain an accurate characterisation of the thermodynamic and kinetic properties of these architectures, with the aim of better understanding their function and potential applications, brought with it the necessity of blocking the formation of extensive and highly ordered β-sheet-like CP assemblies that have undefined and uncontrollable length. This objective was achieved by installing *N*-methyl axial substituents in one of the two faces of the CP monomer.[17] In this manner, only dimeric tubular structures can be assembled. The dimers constitute simple model systems suitable for further characterisation and investigation of more complex self-assembly processes leading to larger tubular structures. α,γ-CPs are cyclic peptide hybrids composed of several units of α- and γ-amino acids that exhibit large dimerisation constants.[18,19] The γ-amino acids are usually constructed using cyclopentane (Acp) or cyclohexane (Ach) scaffolds, as shown in the structures of **CP6** and **CP7**, respectively (Scheme 1).[20] In addition to their tendency to homodimerise (i.e., **CP6·CP6** and **CP7·CP7**), the blocked CPs show significant self-sorting abilities yielding the heterodimeric aggregates in amounts that are significantly larger than expected in a self-sorting process involving isoenergetic dimers (**CP6·CP7** in Scheme 2). Previous reports assigned a 20-fold increase in the thermodynamic stability of the cyclopeptide heterodimer with respect to the parent homodimers.[21] The equilibrium constant for the self-sorting process of the homodimers into the heterodimer assembly is estimated to be 400, which is about one hundred times larger than the statistically predicted value ($K_{SS}=4$; see Scheme 3). This observation was explained by attributing to the heterodimeric assembly the existence of energetically more favourable intermolecular interactions between the backbones of the cyclohexyl–cyclopentyl (Ach:Acp) components than the corresponding ones in the cyclohexyl–cyclohexyl (Ach:Ach) and cyclopentyl–cyclopentyl (Acp:Acp) homodimers.[21,22]



Scheme 2. Binding model used for the calculation of the stability constant of heterodimer **CP6·CP7**. The monomers and dimers are shown in schematic representation. Only the eclipsed regioisomers of the dimers is depicted.

Supramolecular systems bearing photo- and electroactive functionalities are particularly interesting for the development of efficient arrays of chromophores suitable for energy collection and charge separation, which might have potential appli-



Scheme 3. Self-sorting equilibria showing the schematic representation of the eclipsed regioisomer for the heterodimer. The relationship that exists between the equilibrium constant of the self-sorting/disproportionation process and the thermodynamic stability constants of the dimeric assemblies is indicated. Please note that even if homo- and heterodimers were held together by intermolecular forces of analogous strength (same microscopic binding constant) K_{SS} will take a value of 4, owing to the statistical advantage provided by the reduced symmetry of the heterodimer.

cations in artificial photosynthesis.[23–27] In this context, some years ago one of us reported the physicochemical properties of a CP heterodimeric assembly of the type Ach:Acp decorated with complementary electron-active chromophores at its periphery.[28] In brief, a photoexcited fullerene C_{60} unit covalently attached to one cyclopeptidic component of the heterodimer underwent a one-electron transfer process from a π-extended tetrathiafulvalene (exTTF) residue located on the complementary monomer. Unfortunately, the extent of the charge-separation process was quite limited. The main reason being that only one of the three possible regioisomeric heterodimers (eclipsed) was efficient in promoting the process. The other two regioisomers (staggered) were less likely to mediate the electron-transfer process owing to the large distances featured between donor and acceptor units.

Previously, we described the installation of Zn–porphyrin residues in dimeric assemblies of cyclic octapeptides as a way to control the relative distribution of the rotatable regioisomers.[29] The interaction of a bis-Zn–porphyrin homodimer with a ditopic diamine, namely, 1,4-diazobicyclo[2.2.2]octane (DABCO), induces the mixture of regioisomers to adopt exclusively the conformation in which DABCO is sandwiched between two porphyrin moieties. We hypothesised that the combination of a fullerene C_{60} unit with a Zn–porphyrin residue in a dimer of cyclic peptides based on Ach and Acp backbones should yield a thermodynamically highly stable heterodimer that may exhibit interesting physicochemical properties. The interaction between the flat Zn–porphyrin and the curved surface of the fullerenes is known to be attractive and is expected to induce the preferential assembly of the heterodimer as the eclipsed regioisomer (Scheme 2).[30] In addition, the direct "non-covalent" interactions between Zn–porphyrin and fullerenes have important implications for the generation of efficient photoactive architectures. Supramolecular donor–acceptor hybrids containing these units are well known to have the ability to generate charge-separated species by light incidence, thus mimicking the natural photosynthetic process.[31] In general, the construction of supramolecular assemblies decorated with Zn–porphyrin and fullerene residues provides significant synthetic advantages with respect to the covalent construction of closely related dyads.[32]

In this manuscript, we describe the synthesis of two cyclopeptides **CP6** and **CP7** based on Acp and Ach backbones, which are decorated at their peripheries with one Zn–porphyrin and one fullerene residue, respectively (Scheme 1). In solution, CP monomers **CP6** and **CP7** readily self-assemble into homodimeric aggregates **CP6·CP6** and **CP7·CP7**. We disclose our attempts towards the accurate thermodynamic characterisation of the homodimers. We also report on the self-sorting process of the homodimers, which produces the exclusive formation of the heterodimeric hybrid **CP6·CP7**. The **CP6·CP7** dimer bears complementary and photoactive Zn–porphyrin and fullerene chromophores at the periphery of the two adjacent monomers. We also examine in detail the effect that the attractive intramolecular interaction established between the chromophores produces in the distribution of the three possible regioisomers of the **CP6·CP7** heterodimer. Finally, we present the results obtained in the photophysical investigations of the heterodimer demonstrating the existence of a highly efficient intramolecular electron-transfer process. The extent of the process is clearly related to the distribution of regioisomers of the heterodimer. The Zn–porphyrin/fullerene **CP6·CP7** hybrid powers the electron transfer in significantly larger magnitude than the π-extended tetrathiafulvalene/fullerene cyclopeptide-hybrid analogue previously reported.[28] Furthermore, whereas in the former case only the fullerene's excited state was able to yield the charge-separated state, in the present case excitation of any of the two chromophores (C_{60} or Zn–porphyrin) induces the electron-transfer process. The complete characterisation of the photoinduced processes that take place within the heterodimeric assembly **CP6·CP7** in solution is also described. The presented findings are highly relevant both for further understanding the characteristics of the electron-transfer processes occurring in supramolecular systems, as well as for the eventual exploitation of this particular Zn–porphyrin/fullerene **CP6·CP7** hybrid in functional devices.

Results and Discussion

Synthesis

The experimental procedures for the synthesis and the characterisation data of the parent cyclic peptides **CP1**–**4** are described in the Supporting Information (Scheme S1). The compounds were prepared by using procedures that are quite similar to those reported previously.[33] The cyclic peptide **CP5** based on the Acp backbone and decorated with the free-base porphyrin residue was prepared by an esterification reaction (Scheme 1) between **CP3** alcohol and the porphyrin carboxylic acid **1** using *N*,*N*-diisopropylcarboiimide (DIC) as activating agent and a catalytic amount of 4-dimethylaminopyridine (DMAP). The metallation of the porphyrin-substituted cyclopeptide **CP5** was carried out by treatment with zinc acetate in a dichloromethane/methanol mixture yielding the Zn–porphyrin cyclopeptide **CP6** in a 98 % yield after column chromatography purification. The fullerene derivative **CP7** was obtained by amide coupling between the **CP4** amine and phenyl-C61-butyric acid (PCBA), which was activated using *N*-[(dimethylamino)-1*H*-1,2,3-triazolo[4,5-*b*]pyridin-1-ylmethylene]-*N*-methylmethanaminium hexafluorophosphate *N*-oxide (*N*-HATU) and diisopropylethylamine (DIEA) as base in chloroform (Scheme 1). Both CP derivatives, **CP6** and **CP7**, were fully characterised through high-resolution techniques (see the Supporting Information).

It has been shown that fullerene derivatives quite similar to **CP7**[28] and structural analogues of the porphyrin derivative **CP6**[29] display a strong tendency to self-assemble into homodimers when dissolved in non-polar organic solvents. The produced self-assembled homodimers exist in solution as an equilibrium mixture of three possible regioisomers (Scheme 1). We designate the regioisomers as follows: 1) eclipsed isomer (if the larger substituents on adjacent monomers display a *syn* arrangement (**D(S)**)) and 2) staggered regioisomer (when the same larger substituents are located in an *anti* arrangement). In addition, two staggered regioisomers are possible. They can be distinguished by the sense of rotation required for the top CP units to achieve a *syn* arrangement with the larger substituent in the adjacent monomers (clockwise (**D(Acw)**) or counterclockwise (**D(Accw)**)). In solution, the observed molar ratio between staggered and eclipsed regioisomers depends on several factors. Among them, the type of substituents and the nature of the cyclopeptidic backbone are the most important. Based on statistical grounds and assuming that the three regioisomers are isoenergetic, a 2:1 staggered/eclipsed distribution would be expected.

The complexity of the ^{1}H NMR spectrum corresponding to a solution of the porphyrin derivative **CP6** in $CDCl_3$ prevented the accurate determination of the regioisomeric ratio for the dimer **CP6·CP6** but supported its quantitative formation. Conversely, the ^{1}H NMR spectrum of a solution of **CP7** in $CDCl_3$ clearly showed three different doublets for the NH amide proton of the lysine (Lys) side chain resonating at $\delta = 8.44$, 8.42 and 8.29 ppm and also supported quantitative formation of the homodimer. The observation of three separated signals for the NH protons of the lysine side chain indicates the presence of three regioisomeric **CP7·CP7** dimers in solution. The three regioisomers are in an equilibrium that shows slow exchange dynamics on the ^{1}H NMR spectroscopic chemical-shift timescale. Integration of the NH proton signals assigned to each regioisomeric dimer allowed the calculation of the molar ratio of regioisomers **D(Acw)**/**D(Accw)**/**D(S)** as 1:1:2. The fact that the eclipsed regioisomer is the major component in the equilibrium mixture of **CP7·CP7** regioisomers hints to the existence of attractive interactions between the two fullerene residues or, perhaps to the participation of the amide NH of the Lys side chain in a weak hydrogen-bonding interaction in the eclipsed form as denoted by the downfield shift of its signals in the NMR spectrum. This favourable interaction alters the expected statistical distribution and rules out the idea that the steric strain present in the eclipsed isomers should always bias the equilibrium towards the preferential formation of staggered regioisomers.

The ^{1}H NMR spectrum of an equimolar mixture of **CP6** and **CP7** ($\approx$1 mM) in $CDCl_3$ showed several sets of proton signals but none of them coincided with those previously observed for the regioisomeric mixtures of any of the two homodimers (**CP6·CP6** and **CP7·CP7**). Thus, the lack of signals that could be assigned to the protons of the homodimers indicates the exclusive formation of the heterodimer, possibly as a mixture of regioisomers. Considering that the chemical exchange between regioisomers of the homodimers is slow on the ^{1}H NMR spectroscopic timescale, it is sensible to expect that a mixture of regioisomers of the heterodimer should also show slow exchange dynamics. Unfortunately, the complexity of the ^{1}H NMR spectrum assigned to the heterodimer, as a mixture of regioisomers, precludes any precise calculation of the molar composition. The exclusive formation of the heterodimer **CP6·CP7** from an equimolar combination of homodimers is in complete agreement with previous findings for analogous self-sorting equilibria involving cyclopeptide dimers with Acp and Ach backbone scaffolds.[21] Most likely, and as already mentioned above, the hydrogen bonds that stabilise the heterodimeric assembly Acp:Ach are energetically more favourable than those in the respective homodimers. However, the existence of additional attractive interactions between substituents in the heterodimer cannot be ruled out. The exclusive observation of the heterodimeric assembly **CP6·CP7** at 1 mM concentration indicates that the equilibrium constant for the self-sorting process of homodimers can be estimated as $K_{SS} > 10^4$.

Thermodynamic characterisation of the assemblies

Dimerisation-constant values for hexacyclopeptidic homodimers closely related to **CP6** and **CP7** have been previously reported in the literature.[28,21] The magnitudes of the reported constants are in the range of $K_{Dhomo} = 10^5$–10^6 M^{-1}. By using UV/Vis absorption spectroscopy, we performed a dilution experiment of a solution of **CP6** (10^{-5}–10^{-7} M) in dichloromethane. Upon dilution, we expected to observe shifts in the maxima of the bands of the absorption spectra in response to the concentration changes experienced by the monomer **CP6** and the dimer **CP6·CP6**. Unfortunately, the maxima of the absorption bands in the series of UV/Vis absorption spectra registered at different concentrations, as well as the corresponding extinction coefficients, did not experience noticeable changes. This fact complicates the determination of an accurate dimerisation-constant value for **CP6**. The application of the same dilution technique to a concentrated solution of **CP7** in dichloromethane was again unsuccessful for the accurate determination of its dimerisation-constant value owing to the complete lack of spectral changes. In view of these limitations, we decided to simply estimate the values of the dimerisation constant for both **CP6** and **CP7** as $K_{Dhomo} = 1 \times 10^6$ M^{-1}. The magnitude of the estimated dimerisation-constant values is in complete agreement with those previously reported for related cyclopeptides.[28,34] At this point, it is important to highlight that the use of "non-covalent" reversible interactions in the assembly of dimeric molecular aggregates or aggregates of any other stoichiometric order suffers from a strong drawback when compared with the connection of molecular units by covalent bonding. That is, as a result of the use of a molecular self-assembly process, the species involved in the equilibrium will be present in solution in varying amounts. The magnitude of the stability constant of the assembly and the concentration used to perform the self-assembly are key factors in determining the distribution of species in solution. In the case at hand, the magnitude of the dimerisation constants estimated for **CP6** and **CP7** dictates that both monomer and dimeric species will be present in solution, although to a different extent and that the ratio of the dimer/monomer concentrations will depend on the total monomer concentration used.

To assess the relative thermodynamic stability of the homodimers **CP6·CP6** and **CP7·CP7** with respect to the heterodimer **CP6·CP7**, we performed a UV/Vis absorption titration experiment. We used a solution (≈0.7 μM) of the porphyrin derivative **CP6** in dichloromethane, to which we added incremental amounts of a concentrated solution of **CP7** in the same solvent. The concentration of the porphyrin derivative **CP6** was kept constant throughout the titration. The incremental addition of the fullerene derivative **CP7** provoked a significant decrease in the absorption intensity of the Soret band of the porphyrin unit of **CP6** and a concomitant bathochromic shift from 422 to 430 nm (Figure 1a). The titration gave clear isosbestic spectra. The UV/Vis absorption data were analysed mathematically by using a theoretical binding model that considers two species in four coloured states: the monomer of **CP6**,[35] the homodimers **CP6·CP6** and **CP7·CP7** and the heterodimer **CP6·CP7** (Scheme 2). To reduce the number of variables in the fit, the absorption spectra (molar absorption coefficient scale) of the dimers **CP6·CP6** and **CP7·CP7** were fixed to those registered using 10^{-5} M solutions, respectively. At this concentration, the dimer is considered to be the almost exclusive species present in solution for $K_{\mathrm{Dhomo}} = 1\times10^{6}\,\mathrm{M}^{-1}$. The dimerisation constants were also fixed to the values described in the literature for closely related systems ($1\times10^{6}\,\mathrm{M}^{-1}$; see above). The fit of the titration data to the theoretical binding model was good and returned the stability-constant value for the heterodimer **CP6·CP7** as K(**CP6·CP7**)$=1.8\times10^{8}\,\mathrm{M}^{-1}$ (Figure S1 in the Supporting Information). Remarkably, the magnitude of the stability constant for the heterodimer **CP6·CP7** turned out to be one order of magnitude larger than those described/estimated for related Acp:Ach-type heterodimers either with no additional substituents[21] or bearing one fullerene and one exTTF unit[28] covalently attached to the periphery of the CP monomers.

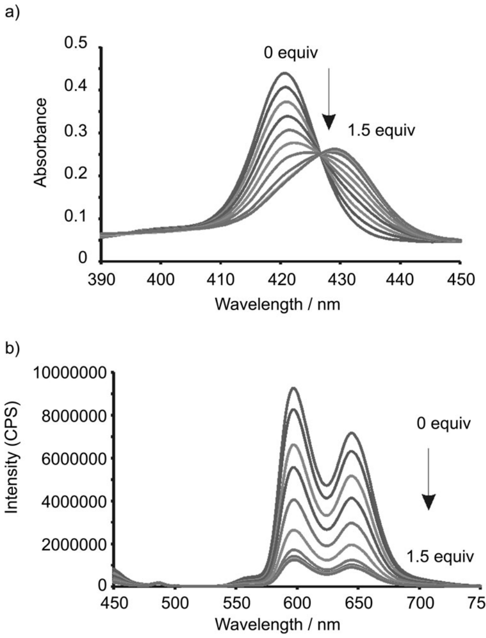


Figure 1. a) UV/Vis absorption and b) fluorescence spectra registered during the titration of [**CP6**]$=7\times10^{-7}$ M with **CP7** (0–1.5 equiv).

The higher thermodynamic stability determined for **CP6·CP7** could be attributed to the existence of attractive interactions between the porphyrin and the fullerene substituents. This hypothesis is supported by the existence of charge-transfer bands in the UV/Vis absorption spectrum of the **CP6·CP7** heterodimer (see below). It is well known that fullerenes form thermodynamically stable complexes with metalloporphyrin dimers[36] and trimers.[37] The additional interactions between C_{60} and the Zn–porphyrin residues will add up to the hydrogen bonds established between the CP backbones of the monomers in the heterodimer, thus providing a sensible increase in the thermodynamic stability of the heterodimeric aggregate.

In any supramolecular complex held together by multiple non-covalent interactions (multivalency), the bound state can consist of a mixture of complexes displaying partially and fully bound geometries.[36,38,39] In the case discussed here, the measured stability constant (macroscopic) for the heterodimer, K(**CP6·CP7**), is considered to be the sum of the stability constants corresponding to the three possible regioisomers (three bound states). We also consider that the eclipsed isomer must correspond to the fully-bound geometry, in which both the hydrogen-bonding interactions established between the cyclopeptidic backbones of the monomers and the fullerene–porphyrin interactions are simultaneously present. However, in any of the two staggered regioisomers, owing to geometrical constrains, the fullerene–porphyrin interaction is less likely. Thus, the calculated value for K(**CP6·CP7**) is shown in Equation (1):

$$K(\mathbf{CP6}\cdot\mathbf{CP7}) = 2\,K_0 + K_0K_1\mathrm{EM} \qquad (1)$$

in which K_0 is a stability constant of a model system for a heterodimer Acp:Ach lacking substituents, K_1 is the association constant for the porphyrin–fullerene interaction, EM is the effective molarity of formation of the intramolecular porphyrin–fullerene interaction and the 2 is a statistical factor that accounts for the degeneracy of two isoenergetic staggered regioisomers. By considering the partially bound state scenario discussed above, it is possible to calculate the relative population of fully bound (eclipsed) and partially bound (staggered) states simply by selecting a reference value for K_0. Unfortunately, an undisputable value of K_0 is not available from previous example in the literature, but it is sensible to assume that it should be close to one order of magnitude larger (≈$10^{7}\,\mathrm{M}^{-1}$) than the dimerisation constants of the homodimers. This magnitude accounts for the more than statistically predicted assembly of the heterodimer Acp:Ach that was experimentally observed in self-sorting processes of equimolar mixtures of homodimers $[Acp]_2$ and $[Ach]_2$ with K_{Dhomo} values of approximately $1\times 10^6\,\text{M}^{-1}$. By using Equation (1), the experimentally determined value for K(**CP6⋅CP7**)$\,=1.8\times 10^8\,\text{M}^{-1}$ and $K_0=10^7\,\text{M}^{-1}$, the population of the staggered isomers (partially bound state) in the heterodimer can be calculated to be $[2K_o/K$(**CP6⋅CP7**)$]\times 100=11\%$. Whereas the eclipsed isomer (fully bound state) must represent the rest of the population of the bound-state: $\{[K$(**CP6⋅CP7**)$-2K_o]/K$(**CP6⋅CP7**)$\}\times 100=89\%$. The use of the partially bound state scenario for the calculation of the distribution of bound states (regioisomers) gives an important weight to the K_0 value used as reference. For example, by simply assuming that $K_0=2\times 10^7\,\text{M}^{-1}$, just a twofold increase with respect to our previous estimate, the calculated distribution of regioisomers turns out to be 22% staggered and 78% eclipsed.[40] The calculation of the percentage of eclipsed and staggered isomers that are present in solution for the heterodimer **CP6⋅CP7** will become more relevant at the end of the section dedicated to the study of its photophysical properties (see below).

The above calculation of the percentage of regioisomers for the **CP6⋅CP7** heterodimer indicates that the eclipsed isomer is highly populated. By having at hand values for the stability constants of homo (**CP6⋅CP6** and **CP7⋅CP7**) and hetero (**CP6⋅CP7**) dimeric assemblies, the calculation of the equilibrium constant value for the self-sorting process of homodimers into the heterodimer is straightforward (Scheme 3).

In complete agreement with the large magnitude determined for the stability constant of the heterodimer, the value of the calculated equilibrium constant for the self-sorting process, K_{SS}(**CP6⋅CP7**)$\,=1.3\times 10^5$, is three orders of magnitude larger than the one we could estimate based on reported data for related equilibria involving Acp and Ach homodimers but lacking substituents involved in attractive/repulsive intramolecular interactions.[21] Clearly, the attractive interactions established between the peripheral substituents (Zn–porphyrin and C_{60}) in the heterodimer **CP6⋅CP7** must be responsible both for the high thermodynamic stability of the complex and for the high population of the eclipsed isomer in the regioisomeric mixture.

We also recorded the emission spectra during the titration of **CP6** with **CP7** by exciting at the isosbestic point (427 nm). The emission spectrum of a solution of **CP6** in dichloromethane ([**CP6**]$\,=0.5\,\mu\text{M}$) displayed two characteristic and well-defined bands at 596 and 642 nm (Figure 1b). The intensity of the fluorescence bands of the **CP6** solution was significantly quenched upon addition of incremental amounts of fullerene derivative **CP7**. This finding together with the observed redshift of the Soret band in the titration monitored using absorption spectroscopy support the existence of porphyrin–fullerene π–π interactions to a significant extent in the structure of the heterodimer **CP6⋅CP7** complex. Probably, these interactions are only present in the eclipsed regioisomer and they facilitate the quenching of the porphyrin chromophore through a photoinduced electron-transfer (PET) process mediated by the fullerene residue. This hypothesis will be demonstrated in detail in the following section through the results obtained from a series of accurate photophysical studies.

It is worth noting that the fit of the fluorescence titration data to the same binding model used for the UV/Vis absorption titration data, but considering only two fluorescent species (**CP6** and **CP6⋅CP6**), returned a stability-constant value for the heterodimer **CP6⋅CP7** complex in complete agreement with that determined in the UV/Vis absorption titration experiment.

Photophysical properties of the individual components and related models

The spectroscopic and photophysical properties of suitable models of the photoactive substituents (zinc tetrapentylphenylporphyrin (ZnTPPP), phenyl-C61-butyric acid methyl ester (PCBM); Figure S4 in the Supporting Information) as well as those of the cyclopeptides **CP6** and **CP7** were determined in dichloromethane. Some of the calculated parameters are summarised in Table 1. The molar absorption coefficients of all species were determined at a $6\times 10^{-6}\,\text{M}$ concentration. In the cases of **CP6** and **CP7**, increasing the concentration by two orders of magnitude did not result in any noticeable change in the values of the molar absorption coefficients and spectral distribution. Similar results were obtained in dilution experiments (see above). These results suggest that in the concentration range of 6–600 μM the registered absorption spectra correspond to the homodimers **CP6⋅CP6** and **CP7⋅CP7**, thereby supporting the estimated values of K_D(**CP6⋅CP6**)$\,=K_D$(**CP7⋅CP7**)$\,>10^6\,\text{M}^{-1}$. It is worth noting that the solutions of the functionalised cyclopeptides **CP6** and **CP7**, containing the corresponding self-assembled homodimers as major species, display slightly broader absorption bands and lower molar absorption coefficients than the reference models ZnTPPP and PCBM (Figure S4 in the Supporting Information). Conversely, at room temperature the emission spectral features and lifetimes of solutions of the functionalised cyclopeptides **CP6** and **CP7**

Table 1. Luminescence properties and energy levels of the excited states of models ZnTPPP, PCBM, **CP6** and **CP7** in dichloromethane.

	295 K			77 K		
	λ_{max} [nm][a]	ϕ_{fl}[b]	τ [ns][c]	λ_{max} [nm][a]	τ [ns][c]	E [eV][d]
CP6	601, 648	0.041	1.6	613, 670, 800[e]	1.7 19.7×10^{6}[e]	2.02 1.55[e]
CP7	707, 783	0.00078	1.3	707, 789	1.4	1.75
ZnTPPP	599, 648	0.040	1.6	614, 669, 808[e]	1.6 17.0×10^{6}[e]	2.02 1.53[e]
PCBM	707, 780	0.00083	1.2	713, 793	1.4	1.74

[a] From corrected spectra. [b] Fluorescence quantum yields calculated against PCBM ($\phi=8.3\times 10^{-4}$ in toluene) and ZnTPPP ($\phi=4.0\times 10^{-2}$ in CH_2Cl_2). [c] Excitation at 560 nm for porphyrins (548 nm for phosphorescence) and at 331 nm for fullerenes. [d] Energy level of the excited state calculated from the luminescence maximum at 77 K. [e] Phosphorescence from triplet excited state.

in dichloromethane, self-assembled in dimeric aggregates, are almost identical to those of the corresponding model references (Figure S5 in the Supporting Information and Table 1). Fluorescence spectra of all these compounds were also determined at 77 K in a glassy dichloromethane matrix (Figure S6 in the Supporting Information). For the porphyrin-functionalised cyclopeptide **CP6** and ZnTPPP, the delayed spectra exhibited a phosphorescence band at 800 and 808 nm, respectively, ascribable to the triplet excited state of the Zn–porphyrin (Table 1 and Figure S7 in the Supporting Information).

Spectroscopic and photophysical properties of CP6·CP7

For practical reasons the photophysical determinations have been conducted at higher concentrations than those used for the determination of association constants. However, it was previously confirmed that the self-sorting process takes place at any concentration. During these experiments, carried out at a 6.5×10^{-5} M equimolar concentration of **CP6** and **CP7**, charge-transfer (CT) bands around 720 nm were detected in the absorption spectrum (Figure S8 in the Supporting Information). These are due to the electronic interactions in the ground state between the porphyrin and C_{60} chromophore in close contact in the **CP6·CP7** complex, and are often reported for arrays containing these chromophores.[41] This confirms the interaction between the two components, at least in some regioisomeric form. Molar absorption coefficients of the order of 10^2, or 10^3 $\text{M}^{-1}\text{cm}^{-1}$ as a maximum, are generally reported for this type of interaction. These figures, with a total absorbance of 0.05 on the CT band of a 6.5×10^{-5} M concentration (Figure S8 in the Supporting Information), would allow one to establish that a large fraction of the partners are interacting, that is, they must be present in the eclipsed conformation. This agrees with the former discussion identifying this conformation as the major one, accounting for almost 80–90% of the **CP6·CP7** heterodimer.

In addition, a series of luminescence experiments in steady-state and time-resolved regime were performed using an equimolar mixture of **CP6** and **CP7** at 1×10^{-5} M concentration in dichloromethane, in which, according to the simulated speciation profiles, the **CP6·CP7** heterodimer represents approximately 95% of the total chromophores present (Figure S2 in the Supporting Information). The luminescence spectra obtained by exciting at 556 nm solutions of **CP6** and the **CP6·CP7** complex in dichloromethane (equimolar mixture of **CP6** and **CP7**) are shown in Figure S9 in the Supporting Information. At this wavelength almost exclusive excitation of the porphyrin chromophore is achieved. The obtained results indicate that there is a residual porphyrin luminescence of the order of 28% for the solution containing the **CP6·CP7** complex compared with that of **CP6**. Excitation of the solution containing the **CP6·CP7** complex at 327 nm, in which photons are absorbed predominantly by the fullerene unit (ca. 70%), leads to a residual fluorescence at 710 nm of about 25% compared with a **CP7** solution under the same conditions (Figure 2a). Taken together, these results indicate that in the solution containing the heterodimer **CP6·CP7** as the main component, a quarter of the total fluorescence of the two chromophores, Zn–porphyrin and fullerene, is not quenched.

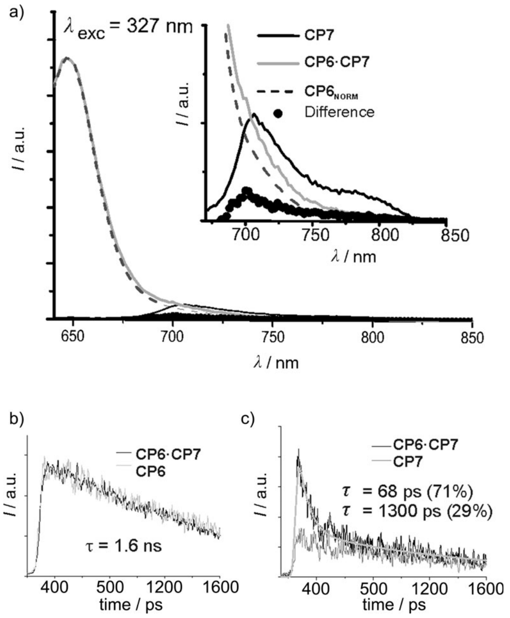


Figure 2. a) Uncorrected emission spectra of **CP7** in CH_2Cl_2 (1×10^{-5} M) and of a solution containing **CP6** and **CP7** in CH_2Cl_2 (1×10^{-5} M) upon excitation at 327 nm. The full dots represent the calculated contribution owing to the fullerene component in the mixture. Inset: magnification of the spectra. b) and c) Integrated streak-camera intensity in the **CP6** emission range, 580–650 nm (b), and in the **CP7** emission range, 740–830 nm (c), after a 35 ps excitation at 532 and 355 nm, respectively.

To better solve the photophysical dynamics of the supramolecular self-sorting process involving homodimers and heterodimer **CP6·CP7**, time-resolved luminescence experiments with nano- and picosecond resolution were performed.

Single-photon-counting determination at 600 nm, after excitation at 560 nm of a 1×10^{-5} M equimolar solution of **CP6** and **CP7** yielded a monoexponential decay with a lifetime of 1.6 ns corresponding to the singlet excited state of the porphyrin chromophore ^{1}**CP6**. Any attempt to also detect by this technique the lifetime of the unquenched fullerene emission in the same solution after excitation at 331 nm failed because of its poor emission properties and overlap with the porphyrin absorption in this region. Streak-camera measurements upon excitation at 532 nm of the same equimolar mixture of **CP6** and **CP7** evidenced again a monoexponential decay of 1.6 ns in the porphyrin fluorescence region (580–650 nm) without any detectable fast component (Figure 2b). In the spectral region of the fullerene emission (740–830 nm), we could observe, upon 355 nm excitation, a weak emission with a biexponential decay (Figure 2c). The derived lifetimes are a short component of 60 ps representing approximately 71% of the decay and a longer one of 1.3 ns accounting for the residual 29%. The latter corresponds to the lifetime of the singlet state of the unquenched fullerene chromophore and represents the fraction of chromophore not liable to quenching. On the basis of the above data we can assume that in the case of the porphyrin chromophore, the quenching detected by steady-state methods has to be ascribed to a reaction faster than the apparatus instrumental resolution, 10 ps, because we are not able to observe it. On the contrary, in the case of the fullerene derivative, the short lifetime of 60 ps can be attributed to a quenching reaction depleting the singlet excited state ^{1}**CP7**. For both chromophores, we could detect decay components with lifetimes identical to that determined for the homodimers of **CP6** and **CP7** (1.6 and 1.3 ns for **CP6** and **CP7** singlet excited states, respectively). This observation confirms the existence of unquenched chromophores in the equimolar solution of **CP6** and **CP7**.

To increase the time resolution, a pump and probe experiment with sub-picosecond resolution was performed. The measured transient absorption spectra at 1 ps after excitation at 550 nm (Figure S10 in the Supporting Information), of an equimolar mixture of **CP6** and **CP7** at 3×10^{-5} M concentration (**CP6·CP7** complex is the major species in solution, ≈95 %) was compared to the one measured from a solution containing only the porphyrin cyclopeptide derivative **CP6** at the same concentration. The two spectra were markedly different (Figure S10 in the Supporting Information). In particular, the spectrum of the solution containing the **CP6·CP7** complex as the major component displays a higher absorbance around 600–700 nm, a typical range for the absorption of the porphyrin cation. From these results, we conclude that the porphyrin cation is already fully formed in the solution containing the **CP6·CP7** complex at 1 ps delay as a consequence of an ultrafast electron-transfer reaction from the porphyrin excited state to the fullerene. No further spectral evolution was registered on the picosecond timescale. This finding increases the limit of the quenching rate of the porphyrin excited state to $k > 10^{12}$ s^{-1}.

Wider timescales were next explored. Transient absorbance in the nanosecond range of the same equimolar solution (3×10^{-5} M, **CP6·CP7** ≈95 %) excited at 532 nm (almost selective excitation of the porphyrin) was registered after a nanosecond flash photolysis experiment (Figure 3). A fast component with a lifetime of 170 ns was detected (left inset Figure 3), with absorption bands around 460–470 nm and 650–680 nm. These latter bands, as mentioned above, are typical for the porphyrin cation. Thus, we ascribe them to **CP6$^{+\bullet}$·CP7$^{-\bullet}$**, the charge-separated (CS) state of the heterodimeric complex resulting from an intramolecular LUMO–LUMO electron transfer from the singlet excited state of the porphyrin to the fullerene. A slower decay on the microsecond scale ($\tau = 20$ μs) with maxima at 480–490 nm and around 600–680 nm is ascribed to the porphyrin triplet (right inset, Figure 3).

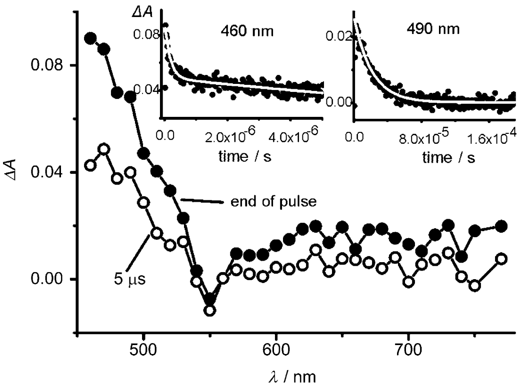


Figure 3. Transient absorption spectra following nanosecond laser flash photolysis at 532 nm in a solution containing [**CP6**] and [**CP7**] $= 3\times10^{-5}$ in CH_2Cl_2. Insets show the time profiles at two representative wavelengths.

When the triplet spectrum corresponding to the equimolar solution of **CP6** and **CP7** is compared, in the wavelength range free from ground-state absorption ($\lambda > 670$ nm), with that measured from a solution of **CP6**, it becomes clear that the bands of the porphyrin triplet excited state are reduced to approximately 25 % in the former (Figure S11 in the Supporting Information). In addition, the porphyrin triplet lifetime of the solution containing **CP6·CP7** is significantly reduced ($\tau = 20$ μs), relative to the lifetime of the porphyrin triplet in **CP6** (180 μs).

A flash photolysis experiment after excitation at 355 nm, in which the fullerene absorbs 50 % of the light, was performed by using an equimolar mixture of **CP6** and **CP7**. A fast decay with $\tau = 180$ ns and centred on 460 and 670 nm can be observed (Figure S12 in the Supporting Information). Like the case described above for the selective excitation of porphyrin, these bands are assigned to the porphyrin cation in the CS state of **CP6$^{+\bullet}$·CP7$^{-\bullet}$**, formed upon HOMO–HOMO electron transfer to the fullerene excited state and decaying by recombination to the ground state. At 2 μs after the flash, both the porphyrin triplet (bands at 470 nm and ≈650 nm) and the typical band of the PCBM triplet (band at 700 nm) were present. The band of the fullerene chromophore is reduced to approximately 20 % with respect to that of the **CP7** solution used as a model (Figures S12 and S13 in the Supporting Information). This observation is in fair agreement with the reduction of the porphyrin triplet signal in the same equimolar mixture and confirms that the parent singlet excited state was reduced accordingly, in agreement with fluorescence data. However, the lifetime for the triplet of the fullerene residue in the equimolar mixture is identical to that determined for **CP7** (13 μs).

Flash photolysis with extended near-infrared (NIR) detection after predominant excitation of the fullerene moiety at 355 nm in an equimolar solution of **CP6** and **CP7** at 3×10^{-5} M was also performed. The transient absorption spectrum (Figure S14 in the Supporting Information) shows typical bands for the fullerene triplet and porphyrin cation together with a weak band around 1040 nm, which is ascribable to the fullerene anion in the CS state of the **CP6$^{+\bullet}$·CP7$^{-\bullet}$** complex. Although the absorbance is rather weak and the signal to noise ratio rather poor, the measured decay lifetime (160 and 200 ns, measured from the two radical bands) is in reasonably good agreement with the previous determinations (see above, 180 ns). This confirms that the CS state **CP6$^{+\bullet}$·CP7$^{-\bullet}$** recombine to the ground state with a lifetime of (180 ± 20) ns and that it is formed upon excitation of both **CP6** and **CP7**.

Molecular modelling studies of CP6·CP7

Simple molecular mechanics studies suggested that both staggered and eclipsed regioisomers of the heterodimeric complex **CP6·CP7** can adopt conformations of similar energy in which the porphyrin and fullerene units decorating their periphery are spatially located at distances allowing direct π–π interaction of chromophores. The shortest separations between a carbon atom of the C_{60} residue and the Zn–porphyrin centre are 2.9 Å (staggered) and 2.8 Å (eclipsed) (Figure S3 in the Supporting Information). More accurate quantum calculations starting from the previous energy-minimised structures were performed with the Gaussian 09 package at the ab initio level of theory (for methods, see the Supporting Information). The shortest separation between a carbon atom of the C_{60} residue and the Zn–porphyrin centre increased in both the staggered and eclipsed conformations up to 3.8 Å. The six hydrogen bonds between **CP6** and **CP7** in the regioisomeric heterodimers are maintained in both structures (Table S2 in the Supporting Information), and whereas the average values are quite similar for both structures (3.051 and 3.042 Å for the eclipsed and staggered conformation, respectively), the hydrogen-bond lengths are more uniform in the eclipsed one, as indicated by their standard deviation (0.031 and 0.067 Å for the eclipsed and staggered conformation, respectively), which suggests a slightly more distorted structure in this latter case. Single-point calculations on the optimised geometries led to an eclipsed regioisomer 6.70 kcal mol^{-1} more stable than the staggered one (see the Supporting Information).

Besides static calculations, molecular dynamics (MD) simulations were performed to analyse the structural and dynamical behaviour of both conformers (40 ns, using explicit chloroform as solvent; for methods, see the Supporting Information). These calculations constitute a powerful tool to analyse the fine details of supramolecular structures, and provide information that cannot be obtained by another technique. The MD simulations starting from a structure in which the chromophores are involved in a π–π interaction (Figure S3 in the Supporting Information) produce an energy-equilibrated structure with the porphyrin and fullerene residues separated by a centre-to-centre distance of (21.2 ± 6.3) Å (Figure 4a). This distance is in agreement with that previously reported from Förster resonance energy transfer (FRET) experiments involving pyrene and Dapoxyl chromophores attached to cyclic peptides.[34] Conversely, MD simulations run starting from the eclipsed regioisomer with the stacked chromophores provided equilibrated structures in which the fullerene and porphyrin residues are much closer together ((6.6 ± 1.1) Å, Figure 4b). In spite of having high root-mean-square deviation (RMSD) values for both regioisomers ((4.04 ± 0.56) and (6.96 ± 1.95) Å for the eclipsed and staggered conformation, respectively), the six hydrogen bonds between **CP6** and **CP7** that can be ideally established between the two monomers are maintained for both conformations. For the eclipsed regioisomer an extra hydrogen bond can be found in more than 50 % of the structures of the trajectory, corresponding to the CO and NH groups present in the side chains of the α-amino acids to which the fullerene and porphyrin units are attached.

Analyses of the different contributions to the energy during the MD simulations suggest that whereas the Coulombic energies for the eclipsed and staggered conformations are very similar, the Lennard-Jones contribution is much more favourable for the eclipsed structure (interaction energies approximately 28 kcal mol^{-1} more stable than for the staggered regioisomer). Cluster analyses for the structures in the trajectory generated from MD simulations led to two representative structures of the most populated clusters for the eclipsed and staggered conformations that are shown in Figure 4. It is worth mentioning that during the MD run, a chloroform molecule is encapsulated early on in the inner cavity of both regioisomers, similarly to what has been described in related studies. The chloroform molecule, once included, remains in the cavity for the duration of the MD simulation.[42] In conclusion, molecular modelling experiments suggest that the fast photoreactivity observed leading to the quenching of the singlet excited states of both chromophores is most likely to occur in the eclipsed regioisomer of **CP6·CP7**.

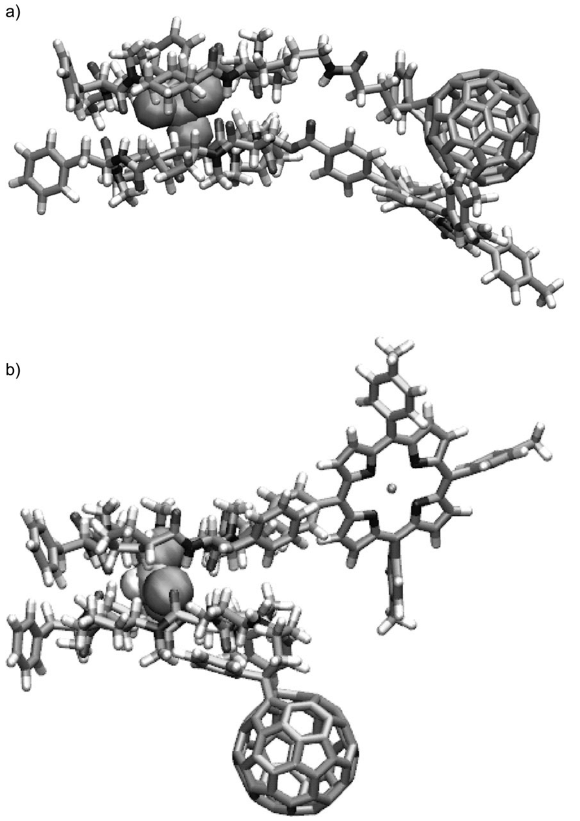


Figure 4. Energy-equilibrated molecular structures produced in the molecular dynamic simulations: a) Eclipsed and b) staggered regioisomers of the **CP6·CP7** complex. It is worth noting that the initial structures for both regioisomers displayed a π–π interaction between the chromophores. See the text for details.

Photoinduced processes within CP6·CP7

Figure 5 depicts an energy-level diagram for the deactivation processes occurring from the two possible singlet states of the **CP6·CP7** complex based on the calculated energies for the singlets and ZnTPPP triplet (Table 1) and on the reported triplet excited state of a methanofullerene related to PCBM of 1.57 eV.[43] The energy level of the CS state corresponding to

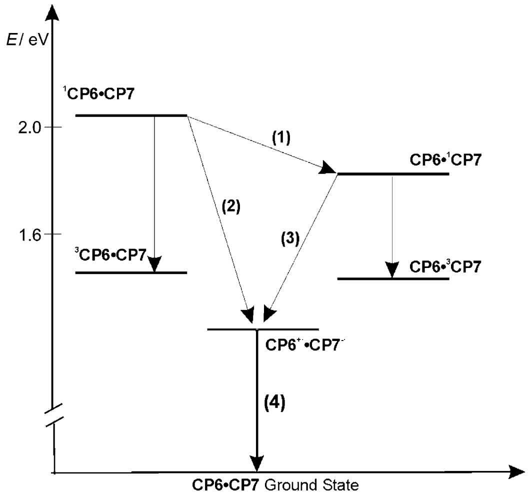


Figure 5. Energy-level scheme and deactivation processes in the complex **CP6·CP7** occurring upon excitation.

the transfer of an electron from the porphyrin to the fullerene unit can be derived from the redox data reported on the literature. PCBM is reduced at -1.08 V versus ferrocene/ferrocenium (Fc/Fc$^+$) in polar solvents,[44] which can be converted to -0.63 V versus the saturated calomel electrode (SCE). The oxidation potential for ZnTPPP was measured as $+0.87$ V versus Ag/AgCl,[45] which converts to $+0.82$ V versus SCE. The energy level of the CS state in dichloromethane can simply be assumed to coincide with the energy necessary to oxidise the donor and to reduce the acceptor, that is, approximately 1.4 eV obtained by adding the two potentials.[46]

The quenching reaction of the fluorescence of the chromophores can be ascribed to either LUMO–LUMO electron transfer (from excited singlet state of the porphyrin to fullerene, step (2)), or HOMO–HOMO electron transfer (from porphyrin to excited singlet fullerene, step (3)). We cannot exclude the occurrence of a parallel intramolecular energy-transfer reaction from the excited singlet state of the porphyrin yielding the excited singlet state of the fullerene, step (1), since it is a spin- and thermodynamically allowed process and therefore might be very fast.

However, the sensitised **CP6·^{1}CP7** state, formed by reaction step (1), reacts with a lifetime of 60 ps to yield the same CS state, step (3), as the excited **^{1}CP6·CP7** state. Therefore, there is very little difference if energy-transfer step (1) is competitive or not. The exceptionally high reactivity of the **^{1}CP6·CP7** state that decays with an overall rate of $k_1+k_2>10^{12}$ s^{-1} compared with that of **CP6·^{1}CP7** ($k_3=1.6\times10^{10}$ s^{-1}) is ascribable to the higher driving force for the LUMO–LUMO reaction step (2) ($-\Delta G^0=0.6$ eV) compared with that of HOMO–HOMO reaction step (3) ($-\Delta G^0=0.35$ eV). In addition, the energy-transfer process (step (1)) might also contribute to the increase of the porphyrin decay. Once formed, the CS state **CP6$^{+\cdot}$·CP7$^{-\cdot}$**, the energy of which is lower than that of both triplet excited states of the chromophores, can only deactivate to the ground state. The ΔG^0 related to the charge recombination is of the order of -1.4 eV, which is sufficiently inverted to display a charge-recombination process in the order of 10^{-7} s, a remarkable lifetime for reaction partners in close contact, but not unusual for fullerene-based arrays.[28,30,47–49]

As stressed above, approximately 25 % of the species in the equimolar mixture of **CP6** and **CP7** survive quenching when excited to the singlet state. These singlet excited states decay unperturbed (as the models) and also lead to triplet excited states **^{3}CP6** and **^{3}CP7**. This also corresponds, roughly, to the observed yield of triplet excited states that survive, which are of the order of approximately 20 %. The triplet excited state of the porphyrin chromophore in solution of pure **CP6** is extremely long lived, 180 μs, and this could allow either inter- and/or intramolecular electron-transfer processes yielding **CP6$^{+\cdot}$** and **CP7$^{-\cdot}$** in solutions containing the two cyclopeptidic derivatives. Interestingly, our results show that the lifetime of the triplet state of the porphyrin is significantly reduced to 20 μs in the equimolar solution of **CP6** and **CP7**. In striking contrast, the **^{3}CP7** state with 13 μs lifetime does not live long enough to react either diffusively or intramolecularly with the porphyrinic chromophore in the heterodimer **CP6·^{3}CP7**. Consequently, the lifetime of **^{3}CP7** is unaltered in the equimolar mixture of **CP6** and **CP7** with respect to that determined for solutions of pure **CP7**.

The assignment of structure to the species/aggregates that do not experience fluorescence quenching in an equimolar mixture of **CP6** and **CP7** is not simple and free of discussion. First of all, we consider that in such a mixture the free monomers and the homodimers, which are in equilibrium with the heterodimer, are not involved in PET quenching processes. However, the sum of free monomers and homodimers can be reasonably set to a maximum of 5 % in the solutions used for the photophysical studies in which the heterodimer constitutes 95 % of the mixture. Thus, we are forced to consider that the staggered regioisomers of the heterodimeric complex **CP6·CP7** are also responsible for the residual observed fluorescence. From the data discussed above, we estimate that the percentage of staggered regioisomers in solution is close to 20 % (0.22 × 95 %). This figure would nicely complement the percentage of monomers and/or homodimers to an overall value of 25 %, thereby providing a plausible explanation to the experimental finding of 25 % residual fluorescence.

The greater distances that exist between chromophores in the staggered regioisomers are unlikely to power any intramolecular PET process. A similar interpretation was already put forward by some of us in explaining the reduced percentage of electron transfer detected in related heterodimers containing fullerene and exTTF chromophores.[28] Fluorescence lifetime measurements of a solution containing the fullerene/exTTF heterodimer as the main component showed a biexponential decay with a 1:2 ratio and lifetimes of <0.1 and approximately 1.5 ns, respectively. The two lifetimes were assigned to the fullerene units experiencing, on one side, electron transfer and on the other, no quenching since the lifetime of the fullerene singlet excited state was unaltered. The ratio of lifetimes fits nicely with the distribution of the regioisomers of the heterocomplex in the ground state, which was determined using ^{1}H NMR spectroscopy as 1:1:1 for the three possible forms.

However, in the study at hand, we observed a significant increase in the electron-transfer process, a 75:25 ratio, occurring in the equimolar mixture of cyclopeptides, compared to the 33:66 described in the aforementioned example. Our results are in line with the formation of the eclipsed isomer in a significantly larger extent. The stability constant of the **CP6⋅CP7** complex is at least one order of magnitude larger than that estimated for the fullerene/exTTF analogue. We explain the increase in thermodynamic stability of **CP6⋅CP7** by making use of the attractive interaction between the two chromophores. This additional interaction has also been claimed to be responsible for distribution populations of eclipsed/staggered regioisomers in the case of **CP6⋅CP7** that are in the range of 90:10 to 78:22 depending on the reference value used for K_0 (see above). The latter distribution ratio fits nicely, as discussed above, with the experimental findings.

It should also be noted that in the present cyclopeptide array, excitation of both chromophores is effective in producing electron transfer, at variance with the aforementioned case in which excitation of the corresponding electron donor, exTTF, was unable to produce electron transfer in any conformation, very likely because of the lifetime (subnanosecond) of the excited state being too short. This fact results in a much higher efficiency in photoconversion upon sunlight illumination for the **CP6⋅CP7** system discussed here.

Conclusion

In summary, we have thermodynamically characterised the self-sorting process leading to the formation of the cyclopeptide heterodimeric assembly **CP6⋅CP7**. The assembled heterodimer bears one electron-donor unit (zinc–porphyrin) and one photoactive electron-acceptor unit (C_{60}) in the two adjacent monomers. A high association constant value ($\approx 10^8\,\text{M}^{-1}$) has been determined for a solution of heterodimer **CP6⋅CP7** in dichloromethane, which hints to the existence of strong interactions between the electron-active groups. Such interaction has been evidenced by UV/Vis absorption and fluorescence spectroscopy titration experiments. In addition, accurate photophysical studies of the solution containing the heterodimer have been undertaken. An efficient photoinduced electron-transfer process, between the porphyrin core and the fullerene moiety, takes place in approximately 80% of the heterodimers **CP6⋅CP7** upon excitation of both chromophores. This yields a radical-ion pair charge-separated state, $\mathbf{CP6}^{+\bullet}\cdot\mathbf{CP7}^{-\bullet}$, with an electron localised on the fullerene unit and a hole localised on the porphyrin component. This charge-separated state has been found to have a lifetime of 180 ns and recombine to the ground state.

The large amount of electron transfer observed in the equimolar mixture of **CP6** and **CP7** (ca. 75%) compared with the previously described counterparts (ca. 33%) is attributed to the preferential assembly of heterodimer **CP6⋅CP7** in an eclipsed conformation for the former, whereas the staggered conformation was preferred in the latter heterodimer. The existence of attractive interactions between the peripheral substituents, C_{60} and Zn–porphyrin, in the heterodimeric cyclopeptide **CP6⋅CP7** powers the energetic advantage of the eclipsed regioisomer. Molecular modelling studies, the calculated distribution of the regioisomers' population using the partially bound state scenario and the determined stability-constant value of the heterodimer **CP6⋅CP7** are also in support of the highly (energetic) preference for the eclipsed versus staggered conformation in this complex.

Acknowledgements

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Keywords: electron transfer · fullerenes · peptides · porphyrinoids · self-assembly

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