Interpretation of Experimental Soret Bands of Porphyrins in Flexible Covalent Cages and in Their Related Ag(I) Fixed Complexes

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1 Interpretation of Experimental Soret Bands of Porphyrins in Flexible 2 Covalent Cages and in Their Related Ag(I) Fixed Complexes

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12 Supporting Information

13 **ABSTRACT:** The essential features of the experimental
14 Soret bands of two covalent cages, consisting of two zinc-
15 porphyrins connected by four flexible spacers, are for the first
16 time interpreted and characterized at a molecular level by
17 means of a mixed quantum/classical procedure based on
18 molecular dynamics (MD) simulation and the perturbed
19 matrix method (PMM). The same method allows also for a
20 comprehensive interpretation of the changes in the UV-
21 visible absorbance of the cages upon silver(I) complexation to
22 the peripheral binding sites. Although the zinc-to-zinc
23 distance is found to be similar in both cages, the MD-PMM
24 calculations show that the conformation adopted by the cage with longer linkers corresponds to more slipped porphyrins, giving
25 rise to a red-shifted (7–8 nm), broader, and slightly split Soret peak with respect to the cage with shorter linkers. The process of
26 silver(I) complexation separates the two porphyrins in a face-to-face conformation in both cages, resulting in narrower (and
27 more similar) Soret bands due to a reduced excitonic coupling. Despite the similar features of the spectra of the two silver(I)-
28 complexed cages, a slight difference in the peak maxima of about 2 nm is observed, arising from a slightly shorter zinc-to-zinc
29 distance in the cage with longer linkers. These results show that the MD-PMM methodology is a reliable method to obtain
30 information on the relative disposition and exciton coupling interaction of porphyrins in flexible systems in solution, from the
31 analysis of their absorption spectra.

32 INTRODUCTION

33 The first steps in natural photosynthesis rely on the collective
34 work of chlorophyll or bacteriochlorophyll organized in
35 antennas to capture light and on their precise arrangement
36 within the reaction centers to convert light energy into
37 chemical energy.^{1–7} The distance and mutual orientation of
38 these chromophores are critical as they determine their
39 absorption range and their efficiency as energy donors or
40 acceptors or as redox active species.⁸ Therefore, engineering
41 systems incorporating porphyrins, tetrapyrrolic macrocycles
42 related to these natural chromophores, has led to various light
43 converting systems.^{9–20} Molecular cages incorporating two or
44 more porphyrins have shown their ability to respond to light
45 and also to work as nanoreceptors or nanoreactors, depending
46 on the specific arrangement and orientation of the porphyr-
47 ins.^{11,21–26} Related to these various applications and as a tool
48 to rationalize and design systems with specific functions,
49 optical spectra of porphyrin architectures can give important

information on the electronic interactions among the single
units, which depend on the geometry of the system. Indeed,
spectral features of the Soret (or B) band of assembled close-
lying porphyrins with strong electronic coupling are largely
affected by the relative position of the monomers. The position
and splitting of the Soret band, which are defined by the
relative orientation of the two B transitions of each
chromophore, B_x and B_y , are commonly qualitatively
interpreted in the frame of the transition dipole exciton
coupling theory.^{11,13,26–31} Nevertheless, a quantitative recon-
struction, and interpretation, of the experimental absorption
spectra of flexible assemblies in solution, such as covalent cages
consisting of two porphyrins connected by four flexible
spacers, is challenging.

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Here, a combined spectroscopic and computational approach is presented to study different flexible porphyrinic cages. Cages 1 and 2 and their corresponding silver(I)-complexed cages, $[\text{Ag}_4(1)]^{4+}$ and $[\text{Ag}_4(2)]^{4+}$, discussed in the present study, are represented in Scheme 1. The four systems

Scheme 1. Chemical Structure of the cages 1 and 2, of Their Silver(I) Complexed Forms (with the Coordination Sphere of Ag(I) Represented as Discussed Below) and of the Reference Compound, Zn-Alkyne

are covalent cages consisting of two zinc(II) tetraphenylporphyrins, Zn-TPPs, connected by four flexible connectors of different lengths, each incorporating two 1,2,3-triazolyl ligands. The linkers of cage 1 that incorporate one ethyleneglycol unit are shorter than the ones of cage 2 that incorporate a diethyleneglycol unit. Binding of four silver(I) ions to the peripheral ligands induces large conformational changes in solution and rigidizes the cages. These conformational changes are reversible: removal of Ag(I) in the presence of an excess chloride anions switches back both cages to their collapsed conformations.^{32,33} The strength of the multimolecular binding process with silver(I) ions is here determined with UV–visible absorption titrations for cages 1 and 2. Absorption and emission properties of the two cages and of their complexes $[\text{Ag}_4(1)]^{4+}$ and $[\text{Ag}_4(2)]^{4+}$ are characterized in solution by means of steady-state and time-resolved spectroscopic techniques.

The computational strategy used in the present work to calculate the UV–visible absorption spectra in the Soret region of the experimentally studied cages is based on the perturbed matrix method (PMM)^{34,35} and molecular dynamics (MD) simulations. With the MD-PMM approach, the Soret band of highly flexible, close-lying porphyrinic assemblies in solution can be reconstructed, allowing a quantitative interpretation of the experimental spectra at an atomic detail. The main strengths of this computational approach are that: (i) a very large number of conformations (including the whole system and the solvent atoms) can be analyzed because the procedure makes use of classical MD simulation for the conformational

sampling; (ii) the effects on the band shape and position arising from the electrostatic perturbation of the environment (i.e., the solvent and the rest of the system, excluding the chromophore) and the excitonic coupling (treated as dipole–dipole interaction) can be separated and their contributions analyzed. The MD-PMM methodology is here applied for the first time to porphyrinic assemblies, the modeling of which is a topic of current and broad interest.³⁶ The very good agreement between experimental and theoretical results gives high credence to this method to get geometrical data of interacting porphyrins in complex architectures, simply from their absorption spectra.

RESULTS AND DISCUSSION

Experimental Results. Absorption and Emission Properties of Cages 1 and 2. The absorption and the emission features of the two cages are characterized in dichloromethane (DCM)/MeOH (90:10) and compared with those of Zn-alkyne (Scheme 1),³² which is considered as a monomeric model for the cages. The absorption spectra of 1 and 2 are shown in Figure 1, together with twice the absorption

Figure 1. Absorption spectra of cage 1 (black), cage 2 (red), and twice the absorption spectrum of Zn-alkyne (gray, dashed) in DCM/MeOH (90:10) in the Soret region ($S_0 \rightarrow S_2$ transition). In the inset, the 480–670 nm region (Q-band region) is shown.

spectrum of Zn-alkyne (the absorption data are collected in Table 1). The Soret bands in the cages are broadened

Table 1. Absorption Parameters in DCM/MeOH (90:10)

	$\lambda_{\text{max}}/\text{nm}$	$\epsilon/10^5 \text{ M}^{-1} \text{ cm}^{-1}$
Zn-alkyne	425	6.37
	557	0.21
	597	0.08
1	419	7.55
	558	0.39
	597	0.16
2	421	5.65
	426	5.83
	558	0.38
	597	0.15

compared to the sum of two model porphyrins, and their features are different in the two cases, showing a splitting in cage 2. The Q-band region (inset of Figure 1), conversely, is nearly identical for 1, 2, and the sum of two Zn-alkyne units. The integrated molar absorption coefficients, calculated on the whole absorption spectrum, are 1.33×10^9 and $1.32 \times 10^9 \text{ M}^{-1}$

126 cm^{-2} for cages 1 and 2, respectively, and equal to twice the
 127 integrated absorption coefficient of Zn-alkyne ($6.62 \times 10^8 \text{ M}^{-1}$
 128 cm^{-2}). This is indicative of exciton coupling within the pair of
 129 identical chromophores in the cages, leading to the observed
 130 spectral features. It can be noticed that although both the Soret
 131 and Q bands arise from transitions from the same molecular
 132 orbitals, the very different magnitudes of the corresponding
 133 transition moments make the Q absorption bands insensitive
 134 to the exciton coupling. A detailed computational analysis of
 135 the origin of the observed spectra is presented in the following
 136 section.

137 Fluorescence spectra, recorded both at room temperature
 138 and at 77 K in DCM/MeOH (50:50), are very similar for the
 139 cages and the model, with maxima at ca. 606 and 660 nm at
 140 room temperature and 600 and 660 nm at low temperature,
 141 respectively, with a slight red-shift for the cages in the latter
 142 case (Figures S1 and S2 and Table S1). Moreover, the
 143 emission quantum yields and the singlet excited state lifetimes
 144 of the cages are almost identical to those of Zn-alkyne (0.040
 145 and 1.7 ns, respectively, Table S1). By means of gated
 146 detection, the phosphorescence spectra of the porphyrins have
 147 been isolated at 77 K, revealing a small red shift (6–7 nm) in
 148 the phosphorescence maxima of the cages compared to the
 149 model (Figure S2 inset and Table S1). The triplet excited state
 150 lifetimes are in the order of 20 ms in all cases. Overall, the
 151 luminescence data indicate that the emission pathways of the
 152 porphyrins are almost unaffected by the constrained environ-
 153 ment of the cage, contrary to what was observed for the
 154 absorption features which are strongly dependent on the
 155 conformation of the systems.

156 **Ag⁺ Complexation of Cages 1 and 2 in Solution.** In order
 157 to characterize the process of complexation of the peripheral
 158 triazole ligands with silver(I) ions, cages 1 and 2 have been
 159 titrated with Ag(OTf) in DCM/MeOH (90:10), after
 160 absorption and emission changes by means of spectropho-
 161 tometric and spectrofluorimetric analysis. Addition of increasing
 162 amounts of Ag⁺ ions to a solution of 2 ($6.1 \times 10^{-7} \text{ M}$) causes
 163 significant modifications in the absorption spectrum of the
 164 cage, as shown in Figure 2. In the Soret region, the splitting is
 165 progressively reduced with depression of the absorption in the
 166 430–440 nm region and increase of a single band at 419.5 nm.
 167 A nearly biphasic behavior is observed, with the isosbestic
 168 point shifting from 425 to 424 nm. The Q-bands are only
 169 slightly affected by the addition of Ag(I) (Figure 2 inset).

Figure 2. Absorption spectra of a solution of 2 ($6.1 \times 10^{-7} \text{ M}$) in DCM/MeOH (90:10) upon addition of Ag(OTf): $[\text{Ag}^+] = 0\text{--}16.5$ equiv (red thick: 0 equiv, blue thick: 16.5 equiv; the arrows indicate the trend of the curves). In the inset, the Q-band region is shown.

Emission spectra, collected upon excitation both at 424 nm
 (isosbestic point of the Soret region, Figure S3) and at 558 nm
 (invariant point of the Q-band region, Figure S4), show a clear
 biphasic trend but with an overall small modification of the
 emission features: in the range 0–10 equiv, a slight intensity
 increase (5–8%) and a 2 nm blue-shift are observed, whereas
 upon further addition of Ag⁺ ions the emission intensity
 decreases by about 10–15%.

Overall, the observed behavior can be ascribed to an initial
 decoupling of the two porphyrins which move apart from their
 initial position after the complexation of the Ag⁺ ions and to a
 subsequent process of formation of a fully complexed
 $[\text{Ag}_4(2)]^{4+}$ cage, where the two porphyrins are forced to stay
 in a remote cofacial conformation. The slight decrease in
 emission intensity is expected on the basis of the “large”
 distance between the two porphyrins in the fully complexed
 cage (0.95 nm, see below). In cofacial porphyrin dimers, in
 fact, the extent of the decrease scales with the decrease of the
 interporphyrin distance, and our data are in agreement with a
 15% reduction of emission intensity previously observed for
 the formation of face-to-face porphyrinic coordination cages
 where porphyrins are held at a distance of ca. 0.70 nm.²⁶ The
 excited state lifetime measured at the end of titration is 1.7 ns,
 similar to that of the uncomplexed cage.

Titration of cage 1 ($4.9 \times 10^{-7} \text{ M}$) with Ag⁺ leads to the
 absorption changes shown in Figure 3: the Soret band

Figure 3. Absorption spectra of a solution of 1 ($4.9 \times 10^{-7} \text{ M}$) in DCM/MeOH (90:10) upon addition of Ag(OTf): $[\text{Ag}^+] = 0\text{--}20.2$ equiv (black thick: 0 equiv, blue thick: 20.2 equiv; the arrows indicate the trend of the curves). In the inset, the Q-band region is shown.

sharpens with the formation of a single band with maximum
 at 421.5 nm. One distinct family of curves with isosbistics at
 404 and 418 nm is observed, defining a single equilibrium of
 complexation. For cage 2, changes in the Q-bands are minimal
 (Figure 3 inset).

Emission spectra, obtained upon excitation at 418 and 556
 nm, show a decrease of intensity on the order of 10%, without
 spectral shift, when the cage is titrated with Ag⁺ (Figures S5
 and S6). This outcome resembles that obtained for cage 2 and
 can be ascribed, as well, to the formation of the fully
 complexed $[\text{Ag}_4(1)]^{4+}$ cage. The extent of the reduction is
 reasonable for a cofacial porphyrin pair at a distance of 0.85
 nm (calculated distance, see below). The measured lifetime for
 the complex is 1.6 ns.

By comparing the absorption spectra of the two cages at the
 end of titration with twice the spectrum of the model Zn-
 alkyne (Figure S7), it can be observed that the spectral shape
 and the intensity of the Soret band is almost (but not fully)

Figure 4. (a) Representative structure of Zn-TTP in which the transition dipoles, μ_{B_x} and μ_{B_y} , are highlighted. Definition of the geometrical parameters defining the reciprocal orientation of the two Zn-porphyrins during the MD simulation of the cages: the distance, R , between the two centers of mass, the angles, θ_1 , θ_2 , that is, the angles between each of the Zn-porphyrin planes and the vector connecting the two centers of mass (b), and β , the angle defining the rotation of the porphyrin planes one with respect to the other (c).

recovered in the complexes (the Soret maximum of the complexes is blue-shifted by 4–5 nm with respect to that of the model). This might confirm that the process of Ag^+ complexation separates the two porphyrins in the cages reducing their exciton coupling. Despite the similar features of the spectra of the two complexes, a slight difference in the peak maxima of about 2 nm is observed. A detailed computational analysis, presented below, clearly describes the origin of the above-mentioned spectral features.

In order to derive the association constants for the formation of the silver(I)-complexed cages, the absorption data have been elaborated by means of the ReactLab Equilibria Software.⁴ The emission data could not be treated due to the small spectral changes observed upon titration. The absorption spectral evolution has been treated assuming a single 1:4 (cage/ Ag^+) equilibrium for both cages. With this model, the fitting of the experimental spectra is reasonably good, even for cage 2, where biphasic behavior has been observed; in the latter, the use of models based on consecutive ($2 + 2\text{Ag}^+ \leftrightarrow [\text{Ag}_2(2)]^{2+}$; $[\text{Ag}_2(2)]^{2+} + 2\text{Ag}^+ \leftrightarrow [\text{Ag}_4(2)]^{4+}$) or parallel ($2 + 2\text{Ag}^+ \leftrightarrow [\text{Ag}_2(2)]^{2+}$; $2 + 4\text{Ag}^+ \leftrightarrow [\text{Ag}_4(2)]^{4+}$) processes did not produce reasonable results.

Figure S8 compares the absorption spectrum of cage 2 with the fitted spectrum of $[\text{Ag}_4(2)]^{4+}$ and the end-of-titration spectrum obtained experimentally. The same comparison for cage 1 is presented in Figure S9. It can be seen that the fitted spectrum of the complex matches well with the experimental one in both cases. The same good correspondence can be observed by comparing the fitted and experimental spectra at different titration stages: Figures S10 and S11 present this comparison for some representative titration points for cages 2 and 1, respectively. The association constants, derived as average of values obtained from the elaboration of different titrations, are [in $\log(K_a/M^{-4})$]: 20.4 ± 0.5 and 20.8 ± 0.9 for 2 and 1, respectively.

Computational Results. Because of large transition dipole moments in porphyrins, modification of their Soret bands upon their assembly within a system are frequently observed. In symmetric metalloporphyrins, this band results from the superposition of two electronic transitions, B_x and B_y , with strong orthogonal transition dipoles in the π -plane degenerate in the monomeric state (μ_{B_x} and μ_{B_y} , Figure 4a). When two porphyrins are placed in proximity, then the first set of transition dipoles, μ_{B_x} and μ_{B_y} , interacts with the second set of transition dipoles of the other porphyrin, μ'_{B_x} and μ'_{B_y} (hereafter, the prime symbol denotes transition dipole moments belonging to the second molecule). The observed absorption band in the Soret region is the sum of the absorption bands resulting from the excitonic coupling. Therefore, in flexible systems in which the orientation of the

assembly is not fixed and has a distribution in space, a broad Soret band is observed due to the presence of various types of interactions among μ_{B_x} , μ_{B_y} , μ'_{B_x} , and μ'_{B_y} .

In what follows, the Soret band of cages 1 and 2 and their corresponding silver(I)-complexed cages $[\text{Ag}_4(1)]^{4+}$ and $[\text{Ag}_4(2)]^{4+}$, are reconstructed and interpreted with the MD-PMM approach. First, one of the systems (namely, cage 2) is used as the model system to investigate changes in the position and shape of the band as a function of geometrical parameters. Then, the spectra of all systems are reconstructed and interpreted.

Uncomplexed Cages 1 and 2. The Soret band of a dimer of Zn-porphyrins (as in the case of the cages) arises from transitions to four exciton states (S_{2a} , S_{2b} , S_{2c} , and S_{2d}). The position and shape of the Soret band, thus, depend on the excitonic coupling between the two Zn-porphyrins (i.e., on the relative intensity of the single exciton states and the magnitude of their splittings) and are, thus, highly sensitive to differences in conformational states. MD simulations and subsequent calculation of the Soret band of cages 1 and 2, thus, allow the characterization of the most probable conformational states for the two cages.

MD simulations of cages 1 and 2 were performed in DCM/MeOH (90:10) at 300 K (1 cage molecule per simulation box, that is, infinite dilution) to reproduce the experimental conditions. From the MD simulations, we identified different conformational states on the basis of the geometrical parameters defining the excitonic coupling, that is, the distance R between the two centers of mass of the two Zn-porphyrins and the relative orientation of the transition dipole moments (Figure 4a), the latter defined by the following angles: θ_1 , θ_2 , the angles between each of the Zn-porphyrin plane and the vector connecting the two centers of mass (Figure 4b), and β , the angle defining the rotation of the porphyrin planes, one with respect to the other (Figure 4c).

In order to choose a reduced number of variables to define the conformational states, we analyzed the dependence of the Soret band on the geometrical parameters mentioned above. In the case of the present cages, β does not vary much and has a negligible effect on the Soret band shape and position (Figure S12). The bidimensional distribution of θ_1 and θ_2 calculated from the MD simulation (see Figure 5) shows a strong linear correlation, indicating that the porphyrin planes tend to be parallel to each other, in particular in the region $\theta_1, \theta_2 > 40^\circ$, in which the planes are more “cofacial”. For $\theta_1, \theta_2 < 40^\circ$ (i.e., for “slipped” conformations), the correlation is lower, indicating the presence of nonparallel (i.e., “oblique”) conformations among the slipped conformations. We tested the dependence of the Soret band as a function of different θ_1 and θ_2 values, both along the $\theta_1 = \theta_2$ diagonal (black) and along the line of equation, $\theta_1 = 65 - \theta_2$ (red), approximating the most

Figure 5. Bidimensional distribution of θ_1 and θ_2 as calculated from the MD simulation of cage 2. A schematic representation of the reciprocal orientation of the two Zn-porphyrins along the black and red diagonal is also reported.

Figure 6. Soret bands calculated on the seven different conformational states identified along the MD simulation of cage 2 and reported in Table 2. (a) Soret bands of states S1, S2, S3, and S4. (b) Soret bands of states C2, C3, and C4. (c) Soret bands of states S2 ($\theta < 40^\circ$) and C2 ($\theta > 40^\circ$) (d). Soret bands of states S3 ($\theta < 40^\circ$) and C3 ($\theta > 40^\circ$). (e) Soret bands of states S4 ($\theta < 40^\circ$) and C4 ($\theta > 40^\circ$). The dashed line shows the position at 424 nm of the band for the monomeric reference.

Concerning the other conformations, the following can be observed: (i) for $0.6 \text{ nm} < R < 0.85 \text{ nm}$ (red curves) and $\theta < 40^\circ$ (slipped conformations), the band has the lowest epsilon and the largest bandwidth (with the peak maximum still showing a slight splitting). (ii) If θ is kept constant, a relative redshift and an increase of intensity (and a resulting narrowing) is observed for increasing R values, the maximum shift being 4–5 nm (see Figure 6a,b); for R values larger than 1.05 nm, the spectrum of the monomeric reference is basically recovered (peak maximum at 424 nm and $\epsilon = 2 \times 5.2 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$). (iii) If R is kept constant, a relative red-shift and a decrease of intensity (and a resulting broadening) is observed for decreasing θ values, the maximum shift being 7 nm at the lower R (see Figure 6c–e).

We used the spectra of the different states to reconstruct the experimental Soret bands of cages 1 and 2. Results are shown in Figure 7. The main results are the following: (i) the spectral features of cage 2 are mainly due to the presence of slipped conformations ($\theta < 40^\circ$) with $0.6 < R < 0.85 \text{ nm}$ (conformation S2 in Table 2); it is worth noting that the X-ray structure of the crystal of cage 2 belongs to the S2 state (the Zn–Zn distance is 0.7 nm and the two Zn-porphyrins are slipped³²); (ii) the spectral features of cage 1 are mainly due to the presence of more cofacial conformations ($\theta > 40^\circ$), whereas the Zn–Zn distance is similar to the case of cage 2 (state C2 in Table 2). The longer linkers of cage 2 ensure more flexibility to this cage, leading to closer porphyrin planes (mean interplanar distance of 0.4 nm) and stronger exciton coupling than in cage 1 with shorter linkers (mean interplanar distance of 0.7 nm).

Cages 1 and 2 Complexed with Ag^+ Ions. In the fully complexed $[\text{Ag}_4(1)]^{4+}$ and $[\text{Ag}_4(2)]^{4+}$ cages, one Ag^+ ion is coordinated to each of the four linkers. The coordination of Ag^+ ions with the linkers was modeled by performing quantum mechanical (QM) calculations on model systems made of a subpart of the system (i.e., one linker) and one Ag^+ ion (see Methods section). The geometrical parameters of the most stable, optimized structures of the silver(I)-complexed linkers are reported in the Supporting Information (Figure S14).

Table 2. Schematic Representation of the Seven States Defined on the Basis of the Geometrical Parameters R and θ

	$R < 0.6$	$0.6 < R < 0.85$	$0.85 < R < 1.05$	$R > 1.05$ (nm)
slipped ($\theta < 40^\circ$)	S1	S2	S3	S4
cofacial ($\theta > 40^\circ$)		C2	C3	C4

In Figure 6 are reported the Soret bands calculated on the subpopulations corresponding to the seven states. In addition, the Soret bands of these states were also calculated, excluding the excitonic coupling in order to have a reference spectrum of a monomeric Zn-porphyrin (similar to the Zn-alkyne model used in the experiments) in which only the effect of the perturbation (i.e., the effect of the rest of the cage and the solvent) is retained. The spectrum of the monomeric reference was almost invariant in the different conformations (peak maximum at 424 nm and $\epsilon = 5.2 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$), thus showing only a moderate effect of the perturbation on the spectral features of the Soret band. The spectra reported in Figure 6 are obtained from the simulation of cage 2. A similar analysis was performed for cage 1 showing an analogous dependence on R and θ .

The “closed” state (S1) shows very peculiar features: the band is blue-shifted (with respect to the peak position of the monomeric reference at 424 nm) and the peak is split.

Figure 7. Experimental (a,b) and calculated (c,d) Soret bands for cage 1 (black) and cage 2 (red) in the absence (a,c) and in the presence (b,d) of Ag^+ ions coordinated to each of the four linkers. The black curve in panel (c) is the Soret band of conformation S2 of cage 1. The red curve in panel (c) is the Soret band of conformation C2 of cage 2. The Soret bands in panel (d) are calculated using the whole configurational space sampled by the corresponding MD simulations. The dashed line shows the position at 424 nm of the Soret band for the monomeric reference. Representative snapshots, extracted from the MD simulations of the four systems, of the conformational states that give rise to the calculated spectra are reported.

The spectra calculated with the MD-PMM procedure on the MD simulations of $[\text{Ag}_4(1)]^{4+}$ and $[\text{Ag}_4(2)]^{4+}$ cages in DCM/MeOH (90:10) are reported in Figure 7b,d. In agreement with the experimental results, the spectra of the complexes are blue-shifted by 3–4 nm with respect to the peak maximum of the spectrum of the monomeric reference (i.e., calculated excluding the excitonic coupling) and are narrower than the spectra of the noncomplexed cages. These spectral features are consistent with geometries in which the porphyrins are stacked (cofacial) and at higher distances than in the noncomplexed cages.

From the molecular structures of the MD trajectories, it is possible to explain the slight shift between the peak maxima of the two cages: it is related to the distance between the two porphyrins, the mean value of the Zn–Zn distance being slightly higher in the complexed cage, $[\text{Ag}_4(1)]^{4+}$ (0.92 nm) than in the complexed cage, $[\text{Ag}_4(2)]^{4+}$ (0.85 nm). This difference is likely due to the difference in the coordination of the Ag^+ ion determined by the presence of the additional $\text{CH}_2\text{--CH}_2\text{--O}$ group in the linker of cage 2, which makes it more flexible with respect to cage 1 allowing the central oxygen atom to enter the coordination sphere of the silver(I) ion. This gives rise to a trigonal geometry in which the distance between the two coordinating nitrogens of the linkers, and the corresponding N–Ag–N angle, is lower in cage 2 than in cage 1, in which, instead, the N–Ag–N coordination motif is more linear (see Figure S14). This difference in the coordination geometry leads to a slightly smaller distance between the two triazoles (the distance between the two terminal carbon atoms of each linker being 0.99 nm in cage 2 and 1.02 nm in cage 1), and, consequently, between the two porphyrins (Figure S14). It must be noticed that the Zn–Zn distance found in the MD simulation of $[\text{Ag}_4(1)]^{4+}$ cage gave a Zn–Zn distance (0.92 nm) in very good adequacy with the one obtained recently from the X-ray crystallographic structure of this complex (9.5 Å).³⁷

METHODS

Absorption and Emission Spectroscopy. Spectroscopic grade DCM and MeOH were from Merck and used as received. Silver trifluoromethanesulfonate ($\text{Ag}(\text{OTf})$), from Sigma-Aldrich, has been stored under argon in a sealed vial in

dark and dry conditions. $\text{Ag}(\text{OTf})$ solutions were used fresh and kept in the dark during the measurements. Solutions of cage 2 were filtered with 0.2 μm membrane filters (Minisart RC4 filters) before each measurement to avoid aggregation issues. Integrated absorption coefficients were calculated by plotting molar absorption coefficients as a function of absorption energy (in wavenumbers) and calculating the area under the curves.

Absorption spectra were recorded with a PerkinElmer Lambda 650 spectrophotometer. Room temperature emission spectra were collected with an Edinburgh FLS920 fluorimeter equipped with a Peltier-cooled Hamamatsu R928 PMT (200–850 nm). Fluorescence quantum yields were evaluated from the area of the luminescence spectra, corrected for the photomultiplier response, with reference to TPP (tetraphenylporphyrin) in aerated toluene ($\phi_f = 0.11$).³⁸ Measurements at 77 K, performed with the same fluorimeter, made use of Pyrex tubes dipped in liquid nitrogen in a quartz Dewar. Gated emission spectra were acquired by using a time-gated spectral scanning mode and a μF920H Xenon flash lamp (pulse width < 2 μs , repetition rate between 0.1 and 100 Hz) as the excitation source. Spectra were corrected for the wavelength dependent photomultiplier response. Triplet excited state lifetimes were measured with the same apparatus in multi-channel scaling mode.

Titration experiments were performed by incremental addition of micro aliquots of stock solutions of $\text{Ag}(\text{OTf})$ (10^{-3} to 10^{-4} M) to a solution of molecular cage ($5\text{--}6 \times 10^{-7}$ M). The final volume added was kept below 10% of the total volume to avoid dilution of the porphyrin. The experiments have been conducted avoiding light exposure of the solutions.

Fluorescence lifetimes were measured by means of an IBH time correlated single photon counting apparatus with excitation at 560 nm. Analysis of the decay profiles against time was performed using the Decay Analysis Software DAS6 provided by the manufacturer.

Estimated errors are 10% on lifetimes, 10% on quantum yields, 20% on molar absorption coefficients, and 3 nm on emission and absorption peaks.

PMM Calculations. The MD-PMM approach is a hybrid quantum/classical theoretical-computational approach, similar in spirit to other hybrid methods,^{39–41} based on MD

simulations and on the PMM. In the MD-PMM approach,^{34,42} the part of the system where the quantum processes of interest occur, that is the quantum center (QC), is treated at the electronic level, and the rest of the system is modeled as an atomic-molecular classical subsystem exerting an electrostatic effect on the QC electronic states. The main difference with other hybrid methods is that in the MD-PMM, the whole system (including the QC) phase space is sampled by classical MD simulations based on typical atomistic empirical/semi-empirical force-fields, allowing an extensive sampling of the QC and environment configurational space. The electrostatic perturbation of the environment is included a posteriori: the electronic properties of the isolated QC (unperturbed properties) are calculated quantum-chemically in vacuum (i.e., in the gas phase) and then, for each configuration generated by all-atoms classical MD simulations of the whole system, the electrostatic effect of the instantaneous atomistic configurations of the environment is included as a perturbing term within the QC Hamiltonian operator. The electronic Hamiltonian operator $\hat{H}$ of the QC embedded in the perturbing environment can be thus expressed via

$$\hat{H} = \hat{H}^0 + \hat{V} \quad (1)$$

where $\hat{H}^0$ is the QC unperturbed electronic Hamiltonian (i.e., as-obtained considering the isolated QC) and $\hat{V}$ is the perturbation operator. In typical PMM calculations, the perturbing electric field provided by the environment atomic charges is used to obtain the perturbation operator, $\hat{V}$ via a multipolar expansion centered in the QC center of mass, r_0 (QC-based expansion⁴³)

$$\hat{V} \simeq \sum_j [V(r_0) - E(r_0) \cdot (r_j - r_0)] q_j \quad (2)$$

with j running over all QC particles (i.e., nuclei and electrons), q_j as the charge of the j th particle, r_j as the corresponding coordinates, V as the electrostatic potential exerted by the perturbing environment, and $E = Z\partial V/\partial r$ as the perturbing electric field.

In the present work, we use a very recent development of the PMM approach including higher order terms by expanding the perturbation operator at each atom of the QC (atom-based expansion).⁴³ Within such an approach, the perturbation operator, $\hat{V}$ is expanded within each N th atomic region around the corresponding atomic center, R_N (i.e., the nucleus position of the N th atom of the QC), providing

$$\hat{V} \simeq \sum_N \sum_j \Omega_N(r_j) [V(R_N) - E(R_N) \cdot (r_j - R_N) + \dots] q_j \quad (3)$$

with j running over all QC nuclei and electron, N running over all QC atoms, and each Ω_N as a step function being null outside and unity inside the N th atomic region. Such an atom-based expansion is here used only for the Hamiltonian matrix diagonal elements, whereas the other Hamiltonian matrix elements are obtained by using the QC-based perturbation operator expansion within the dipolar approximation (eq 2).

At each frame of the MD simulation, the perturbed electronic Hamiltonian matrix is constructed and diagonalized, providing a continuous trajectory of perturbed eigenvalues and eigenvectors to be used for evaluating the QC instantaneous perturbed quantum observable of interest, for example, excitation energies/absorption frequencies.

In case we deal with a set of interacting chromophores, that is, a set of interacting QCs, we must take into account the possible excitation coupling occurring among the QCs. In the present case, the interaction between the electronic excitations localized on each of the two Zn-porphyrin units has to be considered. To this aim, we use an improved implementation, previously applied to the study of the hyperchromic effect in DNA,⁴⁴ in which the perturbed Hamiltonian operator for the two QCs has to be considered

$$\tilde{H} = E_0 \tilde{I} + \Delta \tilde{H} \quad (4)$$

where E_0 is the electronic ground-state energy, and $\Delta \tilde{H}$ is the excitation matrix whose diagonal elements are given by the single chromophore perturbed excitation energies. The non-diagonal elements of the excitation matrix, describing the chromophores quantum interaction, are obtained by truncating the expansion of the chromophore interaction operator at the dipolar term. Thus, the electronic coupling between the two QCs is treated as a dipole–dipole interaction and the k, k' interaction operator is given by

$$\begin{aligned} \hat{V}_{k,k'} = & \frac{q_{T,k} q_{T,k'}}{R_{k,k'}} + \frac{q_{T,k} \hat{\mu}_{k'} \cdot R_{k,k'}}{R_{k,k'}^3} - \frac{q_{T,k'} \hat{\mu}_k \cdot R_{k,k'}}{R_{k,k'}^3} + \frac{\hat{\mu}_k \cdot \hat{\mu}_{k'}}{R_{k,k'}^3} \\ & - 3 \frac{\hat{\mu}_{k'} \cdot R_{k,k} \hat{\mu}_k \cdot R_{k,k'}}{R_{k,k'}^5} \end{aligned} \quad (5)$$

where $\hat{\mu}_k$ is the k th chromophore dipole operator, and $R_{k,k'}$ is the k' to k chromophore displacement vector defined by the corresponding chromophore origins (typically the centers of mass). It has to be noted that the modeling of the chromophore interaction as a dipole–dipole interaction is a reliable approximation only for interchromophoric distances larger than the dimension of the chromophore. In the present case, the smallest interchromophoric distance is 0.55 nm, whereas the size of the chromophore (i.e., the distance between the center of mass and the most external atoms of the chromophore) is on the order of 0.4 nm. Thus, the dipolar approximation is suitable to describe the excitonic coupling between the porphyrins in the cages, allowing interpreting such a coupling in terms of dipole strengths, relative orientation, and distance (see the Computational Results section). Therefore, in the off-diagonal elements providing the chromophore quantum interaction as expressed by eq 5, the perturbed transition dipoles are involved, as obtained by considering the single chromophore embedded in the field produced by the other one (and all rest of the environment). Finally, by diagonalizing the excitation matrix, we obtain the perturbed excitation energies and eigenstates (exciton states).

To calculate the absorption spectrum, once the perturbed frequencies (ν) and transition dipoles ($\mu_{j,i}$) for each exciton state are obtained at each of the N frames of the trajectory, we evaluate the excitation energy distribution using an appropriate number of bins in the frequency space. The excitation energies distribution and the corresponding transition dipoles are then utilized for calculating the molar extinction coefficient, $\epsilon_{0,i}$ for the ground to the i th excited state transition, providing the absorption spectra by the equation

$$\epsilon_{0,i} \simeq \sum_{\nu_{\text{ref}}} \frac{\Gamma_A(\nu_{\text{ref}}) h \nu}{N} \frac{e^{-(\nu - \nu_{\text{ref}})^2 / 2\sigma^2}}{\sigma \sqrt{2\pi}} \quad (6)$$

$$\Gamma_A(\nu_{\text{ref}}) = \frac{|\mu_{0,j}|^2 \nu_{\text{ref}}^2}{6\epsilon_0 c \hbar^2} \quad (7)$$

In these last equations, ν_{ref} , $n(\nu_{\text{ref}})$, and $|\mu_{0,j}|^2$ are the frequency at the center of each bin, the corresponding number of MD frames and mean transition dipole square norm within the bin. Moreover, $\hbar = h/(2\pi)$, where h is the Planck constant, ϵ_0 is the vacuum dielectric constant, c is the light speed, and σ^2 is the variance produced by the semiclassical vibrations neglected in the evaluation of the unperturbed properties. In the present case, the value of σ^2 has been estimated on the basis of the full width at half maximum of the experimental spectrum in toluene,⁴⁵ approximating the vacuum condition. Equations 6 and 7 provide the calculated spectral line shape: the width of the calculated bands (inhomogeneous broadening) is, thus, due to the complete effect of the semiclassical fluctuations of the QC and its environment.

Quantum Mechanical Calculations. To calculate the absorption spectra of cages 1 and 2, and their corresponding silver(I)-complexed cages, $[\text{Ag}_4(1)]^{4+}$ and $[\text{Ag}_4(2)]^{4+}$, the two Zn-porphyrins units were selected as QCs. PMM calculations were performed by considering each porphyrin unit embedded in the field produced by the other porphyrin unit, the four flexible spacers, the Ag^+ ions (when present), and the solvent.

QM calculations were performed on zinc(II) tetratolylporphyrins (Zn-TTPs) (with four *para*-methyl groups on the *meso*-phenyl of the TPP) in vacuo in order to obtain the unperturbed electronic eigen functions to be used in the PMM calculations. A geometry optimization of Zn-TTP was performed in vacuo at the density functional theory (DFT) level⁴⁶ with the Coulomb-attenuated hybrid exchange–correlation functional.⁴⁷ The atomic basis sets were as follows: (i) for the zinc atom the LANL2DZ effective core potential for the inner electrons and a double Gaussian basis set of (5S,5P,5D)/(3S,3P,2D) quality for the valence electrons were used;⁴⁸ (ii) for the hydrogen, carbon, and nitrogen atoms, a standard 6-31+G(d) Gaussian basis set was used.⁴⁹

Time-dependent DFT (TD-DFT) was used with the same functional and basis set for evaluating the properties of the involved excited states. The calculations provided the energies, the atomic charges, and dipole moments of the unperturbed electronic ground state and of the first five unperturbed electronic excited states, besides all ground to excited transition dipole moments necessary for the MD-PMM procedure to be applied. Charges are obtained by fitting the classical electrostatic potential outside the molecule to the corresponding QM potential using the electrostatic potential fit procedure (ESP charges).⁵⁰ All QM calculations are carried out using the Gaussian09 package.⁵¹

To achieve a more meaningful comparison between the experimental and MD-PMM calculated absorption spectra, avoiding disagreements and/or deviations due to inaccuracies of the quantum chemical calculations, the QM calculated magnitude of the transition dipoles corresponding to the Soret band excitations was rescaled on the basis of the experimental values in toluene.⁴⁵ In addition, the QM ground state energy was shifted to reproduce the experimental Soret band excitation energies in toluene. In Table S2 of the Supporting Information, the Soret band excitation energies and transition dipole moments of Zn-TTP, both as obtained from the TD-DFT calculations and after the rescaling based on the experimental data in toluene, are reported.

The same level of theory was used for the geometry optimization and atomic charges calculations performed on the silver(I)-complexed linkers (see below).

MD Simulations. MD simulations of cages 1 and 2 and their corresponding silver(I)-complexed cages, $[\text{Ag}_4(1)]^{4+}$ and $[\text{Ag}_4(2)]^{4+}$, were performed in DCM/MeOH (90:10) to mimic the experimental conditions. The initial structure of the uncomplexed cage 2 was taken from the structure of the X-ray crystal.³² To generate the initial structure for the silver(I)-complexed cage, one of the most open conformations generated along the MD simulation of the uncomplexed cage was taken and the four Ag^+ ions were placed between the two coordinating nitrogen atoms of the linkers; then, this structure was energy minimized using the steepest descent algorithm. The initial structures for both complexed and uncomplexed forms of cage 1 were taken from the crystal structure of the complexed cage (for the uncomplexed simulations, the four Ag^+ ions were removed).³⁷

MD simulations were performed with the GROMACS software package using the GROMOS96 [36] force field. The GROMOS force field parameters for uncomplexed cages 1 and 2 were obtained from the Automated Topology Builder (ATB) database,⁵² with the exception of the partial charges set, obtained from QM calculations (mentioned earlier). For cages 1 and 2 in the presence of Ag^+ ions coordinated to each of the four linkers, the force field parameters for the silver(I)-complexed linkers have been obtained as follows. For cage 2, a QM geometry optimization was performed on a model structure of the linker in the presence of one Ag^+ ion obtained by the above-mentioned energy minimization (see Figure S14). For cage 1, a QM geometry optimization was performed on the silver(I)-complexed linker structure taken from the X-ray crystal (Figure S14). For both cages, the bond lengths and angles, provided by the optimized configuration, were used as geometrical parameters for the subsequent MD simulations. QM-derived ESP charges for the silver(I)-complexed linkers were used. The remaining force field parameters were obtained by analogy with similar already parametrized chemical groups.

The four cages were placed in a dodecahedral box large enough to contain the molecule and at least 1.0 nm of solvent on all sides with a proper number of DCM molecules to reproduce the density of DCM at 300 K and 1 bar (1.33 g/cm³). A proper number of DCM molecules was then substituted with the corresponding number of MeOH molecules to reproduce the experimental DCM/MeOH (90:10) proportion. The force field parameters for DCM and MeOH were taken from the GROMACS topology database. Simulations were carried out in the NVT ensemble at a constant temperature of 300 K using the velocity rescaling temperature coupling.⁵³ The LINCS algorithm⁵⁴ was used to constrain bond lengths and a time step of 2 fs for numerical integration of the equations of motion was used. The particle mesh Ewald method⁵⁵ was used for the calculation of the long-range interactions and a cut-off of 1.1 nm was used. After a solute optimization and a subsequent solvent relaxation, each system was gradually heated from 50 to 300 K using short MD simulations. The trajectories were then propagated for 100 ns for each system. Coordinates are saved at every 1 ps.

CONCLUSIONS

A combined spectroscopic/computational study of two covalent cages consisting of two zinc(II)-porphyrins connected by four flexible linkers, that have different lengths in the two

systems, and the conformational changes induced by binding of four silver(I) ions to the peripheral ligands is reported. The complexation processes are characterized in detail by means of absorption and emission spectroscopy in diluted solutions. The computational MD-PMM procedure used here to interpret the spectroscopic absorption data allows to quantitatively reproduce the essential features of the experimental Soret bands and to characterize the molecular interactions responsible for the changes in the UV–visible absorption.

The Soret band of cage 2 with longer linkers results to be red-shifted by approximately 7–8 nm, broader, and slightly split, with respect to that of cage 1 with shorter linkers. The MD-PMM calculations show that these differences are due to the presence of more slipped porphyrinic planes in the cage with longer linkers, whereas the Zn–Zn distance is similar in both cages (in the range of 0.6–0.85 nm). Upon complexation with the silver(I) ions, it can be observed that the spectral shape and the intensity of the Soret band of both cages almost converge to those of the monomeric reference (in which no excitonic coupling is possible) due to a reduction in the excitonic coupling. This is due to binding of the silver(I) ions, which opens the flattened structures and locks the two porphyrins in a face-to-face disposition. Although the spectral features of both complexed cages are similar, a slight difference in the peak maxima of about 2 nm is observed and can be attributed to a slightly higher Zn–Zn distance in the cage with shorter linkers. It is noteworthy that these structural features are consistent with the reported X-ray crystallographic structures of cage 2³² and silver(I)-complexed cage [Ag₄(1)]⁴⁺.³⁷

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.9b00742.

Absorption, emission, and luminescence data and figures related to computational studies (MD and QM) (PDF)

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

MD, molecular dynamics; PMM, perturbed matrix method; TPP, tetraphenylporphyrin; DCM, dichloromethane; TTP, tetratolylporphyrins

ADDITIONAL NOTE

“ReactLab EQUILIBRIA 1.1—Global Analysis and Reaction Modelling for Chemical Equilibria. Jplus Consulting Pty Ltd.

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