Shape-Persistent Phenylene-Ethynylene Macrocycles Spectroscopy and Dynamics: From Molecules to the Hydrogen-Bonded Organic Framework Material

Eduardo Gomez, Maria Rosaria di Nunzio, Miquel Moreno, Ichiro Hisaki,* and Abderrazzak Douhal*

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ABSTRACT: Shape-persistent phenylene-ethynylene macrocycles are being intensively studied since they are being used for making hydrogen-bonded organic frameworks (HOFs). Here, we report on studies of two expanded macrocycles, Ex-COOH and Ex-COOMe (its methyl ester), in solutions and in the solid state (HOF Ex-*apo* and Ex-*ester*, respectively). For Ex-COOH, the theoretical results suggest the occurrence of an excited-state intramolecular charge-transfer in agreement with the experimental observation. While this event occurs in <200 fs in Ex-COOH in DMF solution, it becomes longer (~2.5 ps) in Ex-COOMe. The formed species in the latter case shows a fluorescence lifetime of 2.02 ns, however for Ex-COOH, we found lifetimes of 0.4, 2.2, and 5.95 ns. Nanosecond-flash photolysis studies of Ex-COOH reveal two triplets having lifetimes of 0.45 and 2 μ s. The ensemble solid studies indicate that their photobehaviors are affected by the presence of different fluorescent emitters. Moreover, at the single crystal level, the emission spectra and decays of washed HOF Ex-*apo* crystals do not depend on the interrogated site. These results provide new insights into the photobehavior of both macrocyclic units of HOF Ex-*apo*. The findings will help for future researches and development of smart devices based on this kind of materials.

1. INTRODUCTION

Porous molecular crystals constructed through intermolecular H-bonds are often called hydrogen-bonded organic frameworks (HOFs).^{1–6} During the past decade, these new materials have attracted the interest of the scientific community due to their exceptional properties and applications.^{7–10} Unlike metal–organic frameworks (MOFs)^{11–15} and covalent–organic frameworks (COFs),^{16–20} which still remain the most studied materials due to their potential application in different fields of science and technology,^{21–24} HOFs are constructed only by organic molecules through non-covalent H-bonding interactions.^{25–28} As any other porous material, both the pore sizes and structures are conditioned by the used linkers or molecular units,⁹ giving the formed network different properties and applicability life in gas storage and separation, explosive detection, and optoelectronics, to cite a few of them.^{25,29–32} For example, the luminescent HOF-1111 (composed by a tetraphenylethylene derivative molecular unit) is able to detect several aromatic compounds, including nitroaromatic explosives.²⁵ Recently, we have reported on the dynamics and spectroscopic studies of two HOFs (CBPHAT-1a and CPHATN-1a), constructed by hexaazatriphenylene derivatives.^{33,34} We showed the occurrence of both proton- and charge-transfer reactions and a remarkable response to HCl vapors.³⁴ Another HOF, based on 4,4',4'',4'''-tetra(2,4-

diamino-1,3,5-triazin-6-yl)tetraphenylethene (HOF-5), has shown a certain character of flexibility, making it a potential candidate for gas adsorption and separation.³⁵ HOFs of large pores or channels capable of encapsulating large molecules, like drugs are being exploited by the scientific community.^{36,37} For example, PFC-1 HOF, can efficiently encapsulate doxorubicin (Doxo) for synergistic chemophotodynamic therapy, showing high therapeutic efficiency and lower cytotoxicity.³⁶ Hence, studying new HOFs with large pore sizes is paramount for their potential use in diverse applications in science and technology.

A few years ago, a new kind of HOFs, based on dehydrobenzoannulenes (DBAs) displaying high planarity and large π -conjugation, have emerged as possible candidates for photonic applications.^{38–40} For example, HOF T12-*apo* displays a long fluorescence lifetime (25 ns) and interesting CIE coordinates (0.42, 0.55), which make it a potential candidate to fabricate white light-emitting diode devices.³² The

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Figure 1. (A) Molecular structures of Nu-Ex, Ex-COOMe, and Ex-COOH. (B) Hydrogen-bonded network of Ex-apo. (C) SEM image of the HOF Ex-apo formed by Ex-COOH.

judicious design of the molecular structure of these DBAs is paramount for the control of the crystallinity and pore size of the HOF governed by H-bonds and π - π interactions between the molecular units.⁴¹ To this end, one can change the pore size and the electronic structure of the core of the fundamental units. Indeed, most of the research efforts have been focused on the synthesis of new HOFs and on the control of their porous structure.^{9,27,30,42,43} On the other hand, the scientific literature is still missing a more comprehensive advance in their photodynamics. Time-resolved (femtosecond to nanoseconds regime) studies of the photoprocesses occurring in HOFs will provide concise information on the photoevents that shape their photobehavior, as it has been done, for example, in silica-based materials and their composites.⁴⁴ In addition to this, further research in this direction will improve the knowledge in the related fields in science and technology. For example, investigating the photophysics and photochemistry of HOFs may lead to the development of HOFs-based optoelectronic devices, sensors, and drug delivery.^{45–47}

Here, we report on experimental and theoretical studies of two new π -conjugated systems, more expanded than DBAs, namely, phenylene-ethynylene macrocycles, Ex-COOH and its methyl ester derivative (Ex-COOMe), in *N,N*-dimethylformamide (DMF) solutions and in the solid state. While the UV–visible absorption and emission spectra of Ex-COOH depend on its concentration, the ones of Ex-COOMe are independent. This suggests the existence of different Ex-COOH species at the ground state (S_0), which are generated by the interactions between its carboxylic acid groups and the DMF molecules. For both molecules in DMF, an intramolecular charge-transfer (ICT) reaction occurs at the S_1 state, which is fast (2.5 ps) for Ex-COOMe and ultrafast (<200 fs) for Ex-COOH. The theoretical results support the H-bond interactions of Ex-COOH with DMF molecules and the occurrence of an ICT process at the S_1 state. The ICT species of the methyl ester derivative have a fluorescence lifetime of 2.02 ns, while those of Ex-COOH show lifetimes of 400 ps, 2.23 ns, and 5.95 ns. The ns- μ s flash photolysis experiments on Ex-COOH in DMF show two triplet lifetimes of 0.45 and 2 μ s. In the solid state, Ex-ester and HOF Ex-apo exhibit ICT reactions producing emitters of different fluorescence lifetimes. HOF Ex-apo exhibits an additional fluorescence lifetime of 4.8 ns as a result of H-bond interactions between the Ex-COOH units forming the crystal structure. Moreover, fluorescence microscopy experiments on washed single crystals indicate that the photobehavior does not depend on the interrogated crystal site. These results provide new findings for a better understanding of the photobehavior of both phenylene-

ethynylene macrocycle-based molecules and related HOFs, and this knowledge may help in the design of new HOFs for potential applications in photonics or drug photodelivery. Our previous reports as well as this one are contributing to the understanding of the spectroscopic properties of these novel HOF materials.^{32–34,47,48}

2. EXPERIMENTAL SECTION

Synthesis and characterization of the molecular building blocks units, Ex-COOMe and Ex-COOH (Figure 1A), and the constructed materials (Ex-ester and HOF Ex-apo) were previously reported.⁴⁹ The anhydrous solvent *N,N*-dimethylformamide (99.8% spectroscopic grade, DMF) was purchased from Sigma-Aldrich and used as received.

The theoretical calculations have been carried out at the DFT level for the ground (S_0) and lowest triplet (T_1) states, whereas the time-dependent DFT (TDDFT) formalism was used to optimize and analyze the lowest singlet excited electronic state (S_1). All the calculations have been performed using the long-range corrected hybrid functional CAM-B3LYP⁵⁰ that minimizes the error of internal CT excitations that would appear at an unphysical too low energy. The basis set used is the split-valence 6-31G(d,p), which adds up polarization (d and p functions) for all the atoms.^{51,52} For Ex-Nu, we have verified that a further increase in the basis set (6-311+G(d,p)) does not significantly modify the results for S_0 and T_1 states. The introduction of diffuse (+) functions leads to the appearance of some lowest electronic excited states with unphysical Rydberg character. Full optimization of the different states has been performed without any symmetry restriction. The solvent (DMF) effect has been introduced through the self-consistent PCM continuum method that defines a cavity of solvent (with a specific dielectric constant) where the molecule (solute) is introduced. The polarization of the molecule by the surrounding DMF solvent is considered in the self-consistent procedure.^{53,54} All the calculations have been carried out using the Gaussian09 suite of programs.⁵⁵ This same methodology was previously proved valid for the analysis of a molecular system similar to the one studied here.⁵⁶ In that work, we also compared the results obtained with CAM-B3LYP against more conventional functionals such as B3LYP or PBE0 by performing calculations on the related Nu-T12 core model. Very similar results were found in the calculations of the lowest excited states. Thus, the problem of unphysical low energy states appears not to be relevant for this family of compounds. For the small Nu-T12 model, we also verified that a larger basis set (6-311G(d,p)) does not appreciably modify the energies of the analyzed electronic

states, and we believe that the methodology used here leads to an accurate picture of the energy diagram of this family of compounds.

Steady-state UV–visible absorption and emission spectra have been recorded using JASCO V-670 and FluoroMax-4 (Jobin-Yvon) spectrophotometers, respectively. For diluted, intermediate, and concentrated samples of Ex-COOH in DMF solutions, the optical densities (ODs) at 355 nm in a 1 cm cell were 0.05, 0.35, and 1.78, respectively.

Picosecond (ps) emission decays were measured using a time-correlated single photon counting (TCSPC) system.⁵⁷ The samples were excited at 371 nm by a 40 ps pulsed diode laser (<5 mW, 40 MHz repetition rate), and the instrument response function (IRF) was ~70 ps. The experimental data were analyzed using the FLUOFIT package (PicoQuant), and the fit procedure is described elsewhere.⁵⁷

The nanosecond (ns) flash photolysis setup has been described previously.⁵⁸ Briefly, it consists of a LKS.60 laser flash photolysis spectrometer (Applied Photophysics) and a Vibrant (HE) 355 II laser (Opotek). To excite the sample, we used the third harmonic output (355 nm). The pump fluence was ~80 mJ cm⁻². As a probe light, we used the output for a 150 W Xenon arc lamp. The light transmitted through the sample was then dispersed by a monochromator and detected by a visible photomultiplier (Applied Photophysics R928), coupled to a digital oscilloscope (Agilent Infiniium DS08064A, 600 MHz, 4 GSa/s). The measured IRF of the system is ~8 ns. All the experiments were performed at 293 K and in a 1 cm cell.

The femtosecond (fs) emission transients have been collected using the fluorescence up-conversion technique.⁴⁷ The system consists of a fs Ti:Sapphire oscillator MaiTai HP (Spectra Physics) coupled to a second harmonic generator and an up-conversion setup.⁵⁹ The oscillator pulses (90 fs, 250 mW, 80 MHz) are centered at 740 nm and doubled in an optical setup through a 0.5 mm BBO crystal to generate a pumping beam at 370 nm (~0.1 nJ/pulse). The polarization of the latter was set to magic angle with respect to the fundamental beam. The IRF of the setup is 200 fs, and with a deconvolution procedure, we can resolve components of ~50 fs.

The fluorescence lifetime imaging (FLIM) measurements were performed on a MicroTime 200 confocal microscope.³² As an excitation source, we used a diode laser (40 ps) with an excitation wavelength of 371 nm. For the anisotropy measurements, the light was passed through a polarizing beam splitter that allows for a simultaneous detection of the parallel and perpendicular signals emission. A G-factor of 1.2, accounting for differences in the detection sensitivity for both polarizations in the setup, was used in the calculation of the anisotropy. The limits for the anisotropy range from -0.5 to 1.0, in which -0.5 corresponds to perpendicular orientation and 1.0 to parallel orientation. The emission signal was collected using a long-pass filter (HQ430LP Chroma).

3. RESULTS AND DISCUSSION

3.1. Theoretical Calculations. For a comprehensive theoretical study of the Ex-COOH molecule, we have also performed the calculations for the pristine core (Nu-Ex; see Figure 1A). The theoretical analysis has been done in the gas phase and taking into account the solvent (DMF) effect.

To begin with, the full optimization of the Nu-Ex system inside a continuum cavity of DMF has been carried out at S_0 ,

S_1 , and T_1 states. Table S1 shows the atomic distances. Practically, these distances do not change from a state to another one, indicating that the geometry of the molecule is practically the same in these electronic states. As we can see in Figure 2A, the geometry of Nu-Ex is not fully planar since the

Figure 2. Frontier molecular orbitals involved in the electronic states of (A) Nu-Ex and (B) Ex-COOH molecules. The molecular structures and the numeration of the atoms used in Tables S1–S4 are shown at the bottom of the figure.

central phenyl groups are slightly out-of-plane, so the molecule does not possess any symmetry. While one of the phenyls is almost in the global plane of the molecule, two of them are about 21° out-of-plane. In this case, the dipole moment is almost null because the phenyl groups have no dipole moment. The loss of symmetry is reflected in the shape of the frontier molecular orbitals: they spread over the full molecule but with different magnitudes along the three sides of the triangle (Figure 2A). The S_0 and T_1 states reflect two main electronic excitations involving the HOMO-1, HOMO, LUMO, and LUMO+1 orbitals. The results also show that all the orbitals implied in the lowest electronic excitations are π -type orbitals. Therefore, the S_1 state has a π - π^* character. Even if Nu-Ex is not fully symmetric, it almost fits to the D_{3h} symmetry group, and symmetry considerations lead to the conclusion that the $S_0 \rightarrow S_1$ transition has a very small oscillator strength. The lack of a high degree of symmetry explains why the oscillator strength (f) is not exactly zero. Moreover, the S_2 state, which has a high probability to be accessed from S_0 , is almost degenerate with S_3 (within D_{3h} symmetry, S_2 would be doubly degenerate). It is worth noting that excitation to S_2 (and S_3) involves the same molecular orbitals as those of excitation to S_1 . Upon geometry optimization at S_1 , there is an increase in the deviation from the planar symmetry. So, S_1 now can be accessed from S_0 as the oscillator strength is larger than 1. Transitions to S_2 and the

almost degenerate S_3 states still have a larger probability ($f > 2$). As expected, T_1 has the same $\pi-\pi^*$ nature as that of S_1 .

Figure S1A shows a schematic representation of the energy levels of the different electronic states of Nu-Ex in DMF. We found that the difference between the S_0 and T_1 states in the gas phase is 61.96 kcal/mol (2.68 eV), while this value in DMF decreases until 56.15 kcal/mol (2.43 eV). The energy gap (5.81 kcal/mol) clearly diminishes upon the introduction of DMF (continuum model), revealing the polarity effect of the solvent molecules surrounding Nu-Ex.

Table S2 shows the values of Mulliken charges of the corresponding carbon atoms including those of the atoms attached to them, where we use the numeration shown in Figure 2A. All the values are always quite small. Moreover, they are also quite similar at the electronic states of the same calculation: gas phase and DMF. We notice also small differences when comparing the effect of the solvent: globally, it increases the charge separation, as expected, but the differences are insignificant. Comparing both triplet states, the charges in the presence of DMF are slightly larger than those in the gas phase. The charges at S_1 are closer to the ones of the triplet, especially when the geometry of S_1 is optimized (last column of Table S2). Interestingly, the value on carbon atom 5 at S_0 in both calculations is relatively large and negative. However, at S_1 and T_1 , the negative charge of carbon atom 5 is smaller, although it is now shared with carbon atom 6, so the sum of charges of carbons 5 and 6 is almost the same at the electronic states. For carbon atom 3, there is noticeable change of the sign upon different electronic excitations (from positive to negative). This change only takes place when the geometry is optimized at the excited state. However, the absolute values of the charges are quite small, so this change may not have any relevance.

We have carried out a similar theoretical study for the larger system, Ex-COOH. The optimized geometry at S_0 shows that the molecule is not planar like Nu-Ex (Figure 2B). Table S3 shows the distances between the atoms at S_0 , S_1 , and T_1 . As we have observed for Nu-Ex, the distances between atoms are not significantly different, suggesting that geometry is not affected by the electronic excitation. However, in this case, the 1,4-phenylene rings are out-of-plane and not symmetrically displaced from the planarity. This leads to an increase in the asymmetry of the molecule in comparison with Nu-Ex. This change is also reflected in the shape of the frontier molecular orbitals (Figure 2B). Again, the vertical Franck–Condon excitation shows a quite small oscillator strength of the $S_0 \rightarrow S_1$ transition ($f = 0.07$). As in the Nu-Ex model, the transition mainly comes from two excitations that involve the HOMO-1, HOMO, LUMO, and LUMO+1 orbitals (Figure 2B). These orbitals are clearly identified as π -orbitals, and so, again, the small transition probability has to be ascribed to the “almost D_{3h} ” symmetry of the molecule. Like the Nu-Ex case, the optimization of Ex-COOH at the excited state leads to a less symmetric geometry, and the final geometry shows a relatively large ($f = 1.59$) $S_0 \rightarrow S_1$ transition, while the transition to S_2 (and the almost degenerate S_3) maintains a clearly larger probability ($f = 2.92$), even though the orbitals involved in the excitations to S_2 and S_3 are the same as those involved in the $S_0 \rightarrow S_1$ transition. This observation will be later demonstrated experimentally with the absorption spectrum, which shows the allowed $S_0 \rightarrow S_1$ transition. The shape of the molecular orbitals involved in the excitation to S_1 leads to predict a quite modest degree of CT upon electronic excitation. All the orbitals

involved in the lowest electronic excitations studied here are clearly identified as π -orbitals. Therefore, in the absence of symmetry, these excitations are symmetry-allowed. The spread of the π -orbitals shown in Figure 2B suggests a possible degree of CT upon excitation, as we will see in the experimental part.

Another consequence of the extended asymmetry of Ex-COOH is that, in this case, the dipole moment is not null, as Nu-Ex, being 7.16 and 7.05 D in the gas phase at S_0 and T_1 , respectively. Curiously, both electronic states have almost equal dipole moments, and this is the main reason why the solvent does not modify the relative energy difference between S_0 and T_1 , being in both situations (gas phase and continuum method DMF media) ~ 55 kcal/mol, contrary to what we observed for the small Nu model. Figure S1B shows a schematic representation of the energy levels of Ex-COOH using the continuum method. As we can see, the energy difference (1.05 eV) between the S_1 and T_1 states is smaller than the one for Nu-Ex (1.49 eV). In DMF, the dipole moments have values of 10.24 D (S_0), 10.27 D (T_1), 10.22 D (S_1 (FC)), and 10.14 D (S_1). Again, these values do not present significant differences, confirming the previous observations.

As for the Mulliken charge analysis, now there are more noticeable charge separations between different parts of the molecule (Table S3, and the numeration of the atoms is shown in Figure 2B). Not surprisingly, the carboxylate groups present large charge separation between the carbon and oxygen atoms. Again, the solvent effect is quite small, usually increasing a little bit the charges but with some exceptions. The negative charge value on carbon atom 5 is still quite high, and it even increases a little bit as compared with the one obtained for Nu-Ex. The S_1 and T_1 states show very similar charges, which are not very much different from the ones of the ground state. This is especially true for the charges on the branches. The charges on the core are also similar and are not significantly different from the ones obtained for Nu-Ex that does not have the “benzoic” branches. It can be then concluded that the enlargement of the molecule does not significantly affect the electronic structure of the core. This is in agreement with the quite similar energies of the different states of both Nu-Ex and Ex-COOH. However, the global molecule is not planar, and the dipole moment changes from almost 0 to 10 D.

An interesting point that has been also theoretically analyzed is the possibility of a direct interaction (H-bond) of Ex-COOH with DMF molecules. In this sense, we have calculated the optimized structure with up to six DMF molecules, H-bonded to Ex-COOH. The analysis of the interaction with only one DMF molecule reveals that, as expected, the interaction implies the acid hydrogen atom of the carboxylic acid of Ex-COOH and the oxygen atom of DMF. When we added one molecule of DMF, we observed a large stabilization of 16.57 kcal/mol (Table S5). By subsequent addition of DMF molecules, we still increase the stabilization until all the acid groups of Ex-COOH are each interacting with one DMF molecule. In this case, we obtained a stabilization of 97.44 kcal/mol. Scheme S1 shows the optimized structure of Ex-COOH interacting with six molecules of DMF. H-bonds between the solute and solvent molecules and related proton-transfer reactions are largely studied from the point of view of theory and experiment.^{60–62} The $O\cdots H\cdots O$ H-bond is quite strong as the $O\cdots H$ distance is 1.60 Å. Figure S1 discloses an additional (weaker) interaction of the hydrogen atom of the CHO group of DMF with the other carboxylic oxygen of Ex-COOH. The $O\cdots H$ distances are now quite longer (2.24 Å), so this additional interaction is

quite weak (and not present for the full six DMF molecules as shown in Scheme S1). In brief, the theoretical calculations of Ex-COOH in DMF suggest that (i) the optimized geometry of the molecule is not planar, making the $S_0 \rightarrow S_1$ transition possible. (ii) An ICT reaction occurs at S_1 . (iii) In DMF, the interactions between the acid groups of Ex-COOH and the solvent molecules stabilize the formed complexes, giving the possibility to a co-existence of different structures. We will use this knowledge for a better understanding of the experimental findings.

3.2. Steady-State Absorption and Emission Studies in Solution. To begin with, Figure 3 shows the UV–visible absorption and emission spectra of Ex-COOMe and Ex-COOH in DMF solutions at different concentrations (ODs at 355 nm are 0.05, 0.35, and 1.78).

Figure 3. UV–visible absorption and emission spectra of (A) Ex-COOMe and (B) Ex-COOH at different concentrations in DMF solutions. The excitation wavelength was 350 nm. For diluted, intermediate, and concentrated samples of Ex-COOH, the ODs at 355 nm are 0.05, 0.35, and 1.78, respectively.

The absorption spectra of both molecules are very similar in shape, having an absorption band with two intensity maxima at 320 and 350 nm. We suggest that these bands reflect the $S_0 \rightarrow S_1$ (350 nm) and $S_0 \rightarrow S_2$ (320 nm) transitions. Previously, similar DBA derivatives, Nu-T12, T12-COOMe, and T12-COOH, have been investigated.⁵⁶ The structural difference between these molecules and those reported in this study is shown in Scheme S2. The UV–visible absorption spectrum of Nu-T12 in a DMF solution was characterized by an intensity maximum at 291 nm assigned to the $S_0 \rightarrow S_4$ transition, while the $S_0 \rightarrow S_{1,2,3}$ transitions are symmetry-forbidden. However, the absorption spectra of T12-COOMe and T12-COOH in DMF solutions displayed a maximum intensity at 325 nm assigned to the $S_0 \rightarrow S_2$ transition.⁵⁶ Based on this, we suggest that the amplification of the core causes a loss of symmetry of the molecule, thus allowing the $S_0 \rightarrow S_1$ transition located at 350 nm for both Ex-COOMe and Ex-COOH, while the peak at 320 nm reflects the $S_0 \rightarrow S_2$ transition. As we have discussed in the theoretical part, this molecule displays a high oscillator strength of both transitions, suggesting that they are permitted and visible in the absorption spectrum. It is worth mentioning that, while the absorption spectrum of Ex-COOMe does not depend on the used concentration, the one of Ex-COOH presents some changes reflected in the intensity of the 320 nm band. In particular, upon increasing the concentration, the 320 nm band decreases in intensity, while the shoulder at 400 nm slightly increases in intensity (Figure 3B). As we have discussed in the theoretical part, the molecules of DMF interact with the acid groups of Ex-COOH, generating new complexed and stabilized structures, which can exist at the ground state. Moreover, we have reported that similar molecules with carboxylic acid groups in the extremes interact

with DMF, generating H-bonded complexes and anionic species.^{47,56} Thus, we suggest that the absorption at 400 nm is due to anionic structures as a result of dilution of Ex-COOH weak acid.

The emission spectrum of Ex-COOMe in a DMF solution is independent on the excitation wavelength and presents two intensity maxima at 415 and 440 nm. The full width at half maximum (FWHM) of intensity is large (3520 cm^{-1}), suggesting that the emission comes from more than one species. The large Stokes shift is $\sim 5000 \text{ cm}^{-1}$, suggesting the occurrence of a reaction in the excited structures. Previously, we assigned this reaction in T12-COOMe to an ICT event, and we believe that it is also happening in excited Ex-COOMe. Moreover, the theoretical calculations on Ex-COOH suggest the possibility of an ICT reaction in its excited state; hence, the same reaction can occur in the methyl ester partner. The emission spectra of Ex-COOH in DMF solutions exhibit a dependence on its concentration (Figure 3B). For the concentrated sample, the spectrum displays intensity maxima at 415 and 440 nm, like its ester methylated derivative, a FWHM of 3300 cm^{-1} , and a Stokes shift of 5500 cm^{-1} . This suggests that the electronic structures of the emitting species are not very different, and the ICT reaction takes place at the S_1 states. However, when the concentration of Ex-COOH is very weak, the band around 415 nm vanishes, while a new band at 480 nm appears. Based on the behavior of the absorption spectrum of Ex-COOH upon dilution (formation of anions), we suggest that this emission band at 480 nm is due to the emission of anionic species. To support this assignment, we added 100 μL of 0.1 M NaOH (in DMF) to 3 mL of a concentrated solution of Ex-COOH in DMF (Figure S2A). The emission spectral shape of the concentrated sample turns immediately to the one obtained for the diluted sample, confirming that the anions are the emitting structures at low concentrations. Moreover, taking into account the real signal of the emission spectra, we can observe that the fluorescence of the anionic species is less intense than the one of the ICT species (Figure S2B).

To further characterize the spectroscopy of Ex-COOMe and Ex-COOH molecules, we have recorded their excitation spectra in DMF solutions (Figure S3). The spectrum of Ex-COOMe is quite similar in maxima and shape to the absorption one, indicating a single ground state origin for the excited species. However, the excitation spectrum of the concentrated sample of Ex-COOH shows a red shift of the intensity maximum compared to the absorption one when the observation wavelength increases. This fact suggests that the red-emitting species absorb in this region, and we assign them to anions. The spectrum of Ex-COOH at an intermediate concentration is practically identical in shape to the absorption one in the 420–600 nm observation range. However, observing at 400 nm (the beginning of the emission spectrum), the diluted sample displays a different spectrum whose intensity maximum is blue-shifted with respect to the absorption one. These species are the ones having established H-bonds with DMF molecules. In brief, the steady-state observations are in agreement with the previous theoretical calculations: (i) the $S_0 \rightarrow S_1$ transition is allowed due to the asymmetry of the molecule. (ii) Different species co-exist at S_0 as a result of the interactions between the acid groups of Ex-COOH and DMF molecules. (iii) An ICT reaction may occur at S_1 .

3.3. Picosecond Time-Resolved Experiments in

Solution. To characterize the ps-ns dynamics and relaxation of Ex-COOMe and Ex-COOH in DMF solutions, we carried out ps experiments exciting at 371 nm and observing at different emission wavelengths (Figure 4).

Figure 4. Magic-angle emission decays of (A) Ex-COOMe, (B) concentrated, (C) intermediate, and (D) diluted samples of Ex-COOH in DMF solutions upon excitation at 371 nm and observation as indicated in the inset. The solid lines are from the best global fits using a multiexponential function. The dashed line is the IRF of the setup. For diluted, intermediate, and concentrated samples of Ex-COOH in DMF solutions, the ODs at 355 nm were 0.05, 0.35, and 1.78, respectively.

concentrated one, the contribution of the shortest component (~ 400 ps) over the whole observation range has a value of $\sim 40\%$, while the one for the 2.2 ns component is $\sim 55\%$. The 5.8 ns component only appears at the reddest part of the emission spectrum with a small contribution of 7%. For the intermediate and diluted samples, the contribution of the shortest component decreases as we move to longer wavelengths, while the one of the 5.8 ns lifetime clearly increases. The 2.2 ns component displays its maximum contribution at 550 nm. When the concentration increases, the contribution of the intermediate becomes more noticeable, being this behavior typical of aggregates. Moreover, being the 2.2 ns lifetime similar to that obtained for Ex-COOMe (2.0 ns of ICT species), we suggest that it is due to the emission of aggregates with an ICT character. This fact is also supported by the large Stokes shift observed from steady-state experiments, as Ex-COOMe. The 400 ps component corresponds to Ex-COOH structures H-bonded to DMF molecules, which can (i) relax to S_0 with a lifetime approximately of 400 ps, (2) undergo an ICT reaction, or (3) suffer a proton transfer (PT) reaction to generate the anionic species, which emits in the reddest region with an emission lifetime of 5.8 ns. Because the anions are also present at S_0 , their excitation generates a population of excited anions within the laser pulse, and as a consequence, the rise time, which should be observed as a result of PT events upon excitation of H-bonded Ex-COOH to DMF, cannot be recorded. The fact that the contribution of the shortest component does not decrease at longer observation wavelengths suggests the occurrence of an additional process, generating the third, longest component (5.82 ns) due to the anions and which are not formed in Ex-COOMe (Table 1). The increase in the contribution of this component with dilution (Ostwald's law) supports its assignment to anionic species.

To further characterize the ps dynamics, we also carried out ps time-resolved emission spectra (TRES) of all the samples (Figure 5). The not normalized TRES are shown in Figure S5.

The TRES of Ex-COOMe are similar to the steady-state one, exhibiting two intensity maxima at 420 and 450 nm. In agreement with the above ps discussion, we observed a small red shift of the peak at 450 nm when the gating time increases, reflecting the ICT process occurrence at S_1 . For Ex-COOH, the TRES of the concentrated sample is the same during the whole gating time window (from 0 to 15 ns), which is in concordance with the ps decays. For the intermediate and diluted sample solutions, the peak at 415 nm at short gating times (< 200 ps) is affected by the Raman signal from the solvent. At the beginning, the emission comes fundamentally from the complexes with DMF and aggregates species, while at longer times, the emission around 500 nm increases due to the anions. Scheme 1 illustrates the observed behavior for emission decays at the different generated species for Ex-COOH and Ex-COOMe.

3.4. Nanosecond (ns) Flash Photolysis Studies in

Solution. It is well known that DBA derivatives display a rich slow photodynamic due to the triplet states.^{56,63,64} To explore to the slow relaxation of the Ex-COOH molecule, we carried out ns flash photolysis upon exciting at 355 nm (OD at 355 nm of 1.78). The selection of the observation wavelengths (425, 520, and 660 nm) were based on previous experiments on a similar molecule, T12-COOH.⁵⁶ Figure 6A shows the selected transient absorption decays of the excited sample

Table 1. Values of Time Constants (τ_i), Normalized (to 100) Pre-exponential Factors (a_i), and Contributions ($c_i = \tau_i \times a_i$) in the Signal Obtained from a Global Multiexponential Fit of the Emission Decays of Ex-COOMe and Different Concentrations of Ex-COOH in DMF Solutions^a

sample	λ_{obs} (nm)	τ_1 (ps) $\pm$ 70 ps	a_1	c_1	τ_2 (ns) $\pm$ 0.2 ns	a_2	c_2	τ_3 (ns) $\pm$ 0.2 ns	a_3	c_3
Ex-COOMe	405	940	56	37	2.02	44	63			
	420		24	13		76	87			
	445		14	7		86	93			
	460		6	3		94	97			
	500		4	2		96	98			
	550		3	2		97	98			
Ex-COOH concentrated	405	410	39	10	2.21	61	90	5.82		
	430		39	10		61	90			
	450		40	11		60	89			
	480		41	12		59	88			
	550		41	10		57	75		2	9
	600		42	13		51	66		7	21
Ex-COOH intermediate	405	390	76	32	2.23	24	68	5.75		
	420		75	32		25	68			
	450		70	26		29	64		1	10
	460		65	22		32	64		3	14
	500		51	12		42	61		7	27
	550		42	8		45	53		13	39
Ex-COOH diluted	600	400	36	6	2.25	43	42	5.95	21	52
	405		92	57		6	18		2	24
	430		80	35		16	41		4	24
	450		51	12		33	43		16	45
	480		37	6		42	44		21	50
	550		22	3		41	32		37	65
	600		20	2		30	21		50	77

^aThe excitation was at 371 nm. For diluted, intermediate, and concentrated samples of Ex-COOH in DMF solutions, the ODs at 355 nm were 0.05, 0.35, and 1.78, respectively.

Figure 5. Normalized time-resolved emission spectra (TRES) of (A) Ex-COOMe, (B) concentrated, (C) intermediate, and (D) diluted samples of Ex-COOH in DMF solutions upon excitation at 371 nm and gating at the indicated delay times. For diluted, intermediate, and concentrated samples of Ex-COOH in DMF solutions, the ODs at 355 nm were 0.05, 0.35, and 1.78, respectively. The emission at ~ 420 nm at the delay time (< 200 ps) is affected by the solvent Raman signal.

Scheme 1. Photophysical Diagram (Not in Scale) Showing the Electronic Transitions, Involved Events and Values of Their Time Constants of (A) Ex-COOMe and (B) Ex-COOH in DMF Solutions

Figure 6. Selected transient absorption decays of Ex-COOH in DMF solution with an OD at 355 of 1.78 under (A) air and (B) nitrogen atmospheres and exciting at 355 nm.

equilibrated in an air atmosphere. Table S6 shows the results from the best fit of the experimental transient decays. The fits of the decays at the three observation wavelengths (425, 520, and 660 nm) give two time constants of ~ 0.47 and ~ 2.0 μ s (Table S6). The contribution of the longest

component decreases at longer wavelengths, while the other one displays the opposite behavior. We suggest that these two states have the same nature, a triplet state. To corroborate this assignment, we carried out experiments under nitrogen and oxygen atmospheric conditions (Figure 6B and Figure S5, respectively). As we can see, the decays become longer and shorter under nitrogen and oxygen atmospheres, respectively, than the ones under air conditions, confirming that the involved states are T_1 . For the decays recorded under nitrogen, we obtained time constants of 285 and 1140 μ s. Based on the contributions of both time constants, we suggest that the 2 μ s (obtained under air conditions, and whose contribution decreases at longer wavelengths) and the 0.45 μ s (obtained under air conditions and whose contribution increases at longer wavelengths) components correspond to the 285 and 1140 μ s components, respectively. The large increase between the component under air (0.45 μ s) and nitrogen (1140 μ s) atmospheres can be ascribed to very efficient interactions (collisions and energy transfer) between this triplet state and the oxygen molecule in DMF solution. The fits of the decays under an oxygen atmosphere give values of $\sim$ 90 ns and 2 μ s. While the shortest component appears in the three observation wavelengths; the longest one only appears at 425 nm. We suggest that the species with a time of 2 μ s (which contributes mainly in this observation wavelength) interacts strongly with the oxygen molecule under air conditions; therefore, when we add more oxygen, this triplet state is not affected. However, when its contribution to the decay is very small (at 520 and 660 nm), the 0.45 μ s component is largely affected by the presence of oxygen, reflected as a short decay. Probably, this time is a mixture of both state lifetimes.

3.5. Femtosecond Time-Resolved Experiments in Solution. To characterize the ultrafast photodynamics of both molecules in DMF solutions, we recorded the femtosecond (fs) emission decays of Ex-COOMe and of Ex-COOH in DMF upon excitation at 370 nm (Figure 7 and Figure S5). While Figure 7A,B shows the decays at short time window,

Figure 7. Representative fs emission transients in a short time window of (A) Ex-COOMe and (B) concentrated sample (OD (355 nm) = 1.78) of Ex-COOH in DMF solutions upon excitation at 370 nm. The observation wavelengths are indicated in the inset. The solid lines are from the best fits using a multiexponential function, and IRF is the instrumental response function.

Figure S6 displays the ones at a longer one. Table 2 exhibits the results from the best fits of the experimental decays.

Table 2. Values of Time Constants (τ_i) and Normalized (to 100) Pre-exponential Factors (a_i) of the Function Used in Fitting the fs Emission Transients of Ex-COOMe and a Concentrated Sample (OD (355 nm) = 1.78) of Ex-COOH in DMF Solutions upon Excitation at 370 nm^a

sample	λ_{obs} (nm)	τ_1 (ps) $\pm$ 0.5 ps	a_1	τ_2 (ps)	a_2
Ex-COOMe	425	2.02	7	950*	93
	450				100
	480	2.18	−100		100
	500	2.49	−100		100
	520	2.70	−100		100
Ex-COOH concentrated	425	3.15	17	400*	83
	440	3.10	14		86
	460	3.20	14		86
	480	3.31	13		87
	500	3.42	8		92
	520				94
	540				90

^aThe negative sign for a_i indicates a rising component in the emission signal. The asterisk indicates a fixed value in the fit.

The fs emission decays of Ex-COOMe exhibit a biexponential behavior with time constants of 2–2.7 ps and 950 ps. The shortest component is decaying at the bluest part of the emission spectrum and rising from 480 nm. The longest component is fixed in the fit using the value obtained in the ps experiments. It is well known that vibrational cooling (VC) and solvation of similar molecules in solution occur in the fs-ps regime.^{65–67} In addition to that, we have suggested in the previous parts that Ex-COOMe undergoes an ICT reaction. The rising component of 2.5 ps can also reflect this event. Hence, the 2.5 ps time should be a combination of VC, solvation, and ICT reactions.

For Ex-COOH in DMF, we were able to carry out fs experiments only using the concentrated sample due to the impossibility to obtain clear decays from diluted samples. The best fits of the experimental data in the 425–500 nm observation range reveal a short decay time of 3.1–3.4 ps and a longer one of 400 ps fixed in the fit using the ps data (Figure 7B and Table 2). The short component has a larger contribution than that found for the transients of Ex-COOMe, suggesting the occurrence of a short additional event in the former. As we discussed above, Ex-COOH in DMF can undergo a PT reaction producing anions. Thus, the short component may comprise VC, solvation, ICT, and PT reactions. Unfortunately, for wavelengths longer than 520 nm, the decay did not show any rise, which could be directly assigned to the presence of ICT and PT reactions. One reason of this lack in the recorded signals could be the presence of fast decays (different than VC and ICT) of the anions at longer wavelengths cancelling the expected rise in this region.

Scheme 1 summarizes the unraveled photodynamics of both molecules in DMF solutions. Upon excitation at 370 nm, Ex-COOMe undergoes an ICT reaction in 2.5 ps, which produces ICT species with a fluorescence lifetime of 2.02 ns. The fluorescence lifetime of the initially excited species is 940 ps. On the other hand, a diluted sample of the formed H-bonded complexes undergoes ICT and PT reactions ($\sim$ 3 ps),

generating ICT species and anions, which display fluorescence lifetimes of 400 ps and 5.8 ns, respectively. In addition to this, we also suggest the existence of aggregates, which undergo the ICT process (~ 3 ps), generating ICT species with a lifetime of 2 ns.

Comparing the behaviors of Ex-COOMe and Ex-COOH with those of previously studied analogous molecules (T12-COOH and T12-COOMe) in DMF, we observe that expanding the core of the molecular units largely changes the photobehavior of the spectrum. T12-COOMe shows emission from the triplet state (24.5 ns), while Ex-COOMe does not, however, emitting from an ICT state. The emission of T12-COOH has its maximum intensity at 607 nm, while Ex-COOH displays it at 480 nm. Both T12-COOH and Ex-COOH form H-bonds with DMF molecules, leading to the formation of the anions in Ex-COOH, but not observed in T12-COOH. This reflects a different acidity of the COOH groups in both molecules.

3.6. Steady-State and Picosecond Time-Resolved Emission in the Solid State. After exploring the photo-behavior of the fundamental molecular units of Ex-COOMe and Ex-COOH, we characterized their spectroscopy and dynamics in the solid state, namely, **Ex-ester** and **Ex-apo** (Figure 8).

Figure 8. (A) Emission spectra of **Ex-ester** and **Ex-apo** in the solid state. The excitation wavelength was 380 nm. (B, C) Excitation spectra of (B) **Ex-ester** and (C) **Ex-apo** in the solid state at the indicated observation wavelengths.

Figure 8A shows the recorded emission spectra of **Ex-ester** and **Ex-apo**. While the former is constructed by the COOMe molecules, **Ex-apo**, a HOF, is made by H-bond interactions between the Ex-COOH molecular units. Figure 1B shows the network of the formed HOF and the interaction between the acid groups of the Ex-COOH molecules. The emission spectra of both **Ex-ester** and **Ex-apo** display intensity maxima at 465 and 475 nm, respectively. The excitation spectra collected at different observation wavelengths are similar, indicating a common ground-state origin of the emitters (Figure 8B,C). The intensity maximum of the excitation spectrum of **Ex-ester** is at 418 nm, while that of **Ex-apo** is at 435 nm. This spectral shift of 930 cm^{-1} reflects the effect of the H-bonds in the HOF (Figure 1). The smaller

shift in emission at 450 cm^{-1} suggests the occurrence of a large electronic change in **Ex-ester**.

To explore the photodynamics of the excited species in the solid state, we carried out ps emission experiments on both materials (Figure 9).

Figure 9. Magic-angle emission decays of (A) **Ex-ester** and (B) **Ex-apo** in the solid state upon excitation at 371 nm and recording at the indicated wavelengths. The solid lines are from the best global fits using a multiexponential function, and the dashed line is the IRF of the setup.

To begin with the **Ex-ester** sample, Figure 9A shows the emission decays, and Table 3 gives the obtained results from the best global fits. We got emission lifetimes of 200 ps, 870 ps, and 3.00 ns. All the components are decaying over the explored spectral range (405–550 nm). Clearly, the decays are faster at shorter wavelengths and vanish at ~ 2 ns after excitation (Figure 8A). The shortest component presents its maximum contribution (51%) at the bluest part of the spectrum, while the other two components increase their contributions at the reddest one. Based on the results and discussion of the molecular units in solution, we suggest that the 200 ps component is due to the emission of the initially excited species, while the other components are assigned to different ICT structures generated after an ICT reaction. We observed different lifetimes due to the heterogeneity of the material and the possibility of having different conformers of the methyl ester groups, leading to different characters of ICT within the emitters. Note that the formed **Ex-ester** solid is amorphous. Previously, we have reported on a comparable material (**T12-ester**) in the solid state, observing two emission lifetimes due to the formation of different CT species (5 and 20 ns).^{32,56}

Figure 9B shows the emission decays of HOF **Ex-apo** in the solid state upon excitation at 371 nm, while Table 3 gives the results from the best global fits. We obtained lifetimes of 100 and 420 ps and 1.43 and 4.80 ns. We could not get an accurate fit using three components, as it was the case for the **Ex-ester** sample. The decays are shorter at the blue side of the emission spectrum, and no ps rising component was recorded. While the shortest lifetime decreases its contribution at the reddest part of the spectrum, the longer ones exhibit the opposite behavior. The emission decays of both materials

Table 3. Values of Time Constants (τ_i), Normalized (to 100) Pre-exponential Factors (a_i), and Contributions ($c_i = \tau_i \times a_i$) in the Signal Obtained from a Global Multiexponential Fit of the Emission Decays of Ex-ester and Ex-apo in the Solid State^a

sample	λ_{obs} (nm)	τ_1 (ps) $\pm$ 30 ps	a_1	c_1	τ_2 (ps) $\pm$ 70 ps	a_2	c_2	τ_3 (ns) $\pm$ 0.2 ns	a_3	c_3	τ_4 (ns) $\pm$ 0.3 ns	a_4	c_4
Ex-ester	405	200	80	51	870	19	41	3.00	1	8			
	425		78	48		21	43		1	9			
	450		73	35		25	51		2	14			
	475		60	21		35	56		4	23			
	500		55	17		38	52		7	31			
	525		50	14		40	50		10	36			
	550		44	11		43	46		13	43			
	550		44	11		43	46		13	43			
Ex-apo	430	100	84	50	420	14	34	1.43	2	16	4.80		
	450		74	36		27	52		2	12			
	475		66	28		30	53		4	19			
	500		60	20		33	44		5	24		1	12
	550		52	11		33	27		12	34		3	28
	600		25	3		42	19		27	44		6	34
	650					58	23		35	46		7	31

^aThe excitation was at 371 nm.

exhibit the same trend, and the lifetimes of the three short components of the HOF have half values of those of the Ex-ester, suggesting that the radiative rate constant in the former are twice higher than in the latter (supposing that the radiative lifetimes are the same for both materials). In addition to this general trend, the decays of the former show a 4.80 ns component at the green-red spectral region. Based on the molecular structure of the HOF and on the discussion of the involved H-bonds units in the photodynamics of the molecular units of the HOF, we assign this lifetime to the anions emitters. Following the same scenario for Ex-ester, we assign the 400 ps component to the emission of the initially excited molecular units, while the intermediate ones (420 ps and 1.43 ns) could be due to the fluorescence of different ICT species. Previous reports on the photobehavior of HOFs compared to those of their amorphous partners support our assignment.^{32,34,48} Scheme 2 illustrates the observed results and related assignments for both Ex-ester and Ex-apo photobehaviours in the solid state. Because the time resolution of the ps setup is about 15 ps, we believe that the ICT events in both materials are shorter than this time.

Scheme 2. Photophysical Diagram (Not in Scale) Showing the Electronic Transitions, Involved Events and Values of Their Time Constants of (A) Ex-ester and (B) Ex-apo in the Solid State^a

^aThe green arrows are from fluorescence of the initially excited species, the orange ones from the ICT species, while the red one is from the anionic species of HOF Ex-apo.

3.7. Confocal Microscopy Fluorescence and Time-Resolved Studies. To explore the effect of possible defects and orientation of the molecular units on the photodynamics of this HOF, we performed ps confocal fluorescence microscopy studies of single crystalline particles of Ex-apo (Figure 10).

Figure 10. (A) FLIM, (B) emission spectra at different points, and (C) emission decays at the selected spectral range using a 460 nm long-pass filter of unwashed Ex-apo crystals. The solid lines are from the best fit using a multiexponential function. (D) Histogram of the emission anisotropy. The excitation wavelength was 370 nm.

Figure 10A shows the fluorescence image (FLIM) of crystals of around 15 μm in length. From the color distribution, a large green with a very small contribution of blue, we suggest that the fluorescence lifetimes are the same over the crystals. In the blue region, the contribution of the shortest fluorescence lifetime is larger than in the green one. Figure 10B displays the emission spectra at different selected points of the same crystals. We observe that the intensity of the peak at ~ 425 nm and the FWHM of the emission band change with the recording position, possibility due to chemical or physical defects on the crystals. Other crystals have been interrogated

(Figures S7 and S8) and show a similar behavior, in agreement with to other HOF spectroscopic studies.^{34,48} To shed more light on this behavior, ps time-resolved emission experiments on the same points of the crystals were carried out (Figure 10C). The results show a small difference between the explored points of the crystal. Table S6A displays the data from the best fits, while Table S7A shows a summary of the obtained time constants and pre-exponential factor. Practically, all the points exhibit a biexponential behavior with time constants of 400 ps (90%) and 3 ns (10%), although there are few zones where these time values increase to 600 ps (90%) and 4.5 ns (10%). Based on the ps experiments on bulk and ensemble of crystals, we suggest that the longest fluorescence lifetime is attributed to species having H-bond interactions, while the shortest one could be affected by (physical or chemical) defects or CT species. Physical defects can be observed in the SEM image as cracking in the crystals. In Figure 1C, we can see crystals with different shapes and lengths. It is worth mentioning that large crystals also display attached or adsorbed to their surface small ones, making the heterogeneity of the system complex. To eliminate these small and adsorbed crystals on the large ones, we washed the sample with diethyl ether (Figure 11) and acetone (Figure S9).

Figure 11. (A) FLIM, (B) emission spectra at different points, and (C) emission decays at the selected spectral range using a 460 nm long-pass filter of **Ex-*apo*** crystals washed with diethyl ether. The solid lines are from the best fit using a multiexponential function. (D) Histogram of the emission anisotropy. The excitation wavelength was 370 nm.

Clearly, the emission spectra do not depend on the interrogated site on the crystal, contrary to the behavior on the unwashed ones (Figure 10B). Thus, upon washing, we could eliminate small crystals and possibly molecules adsorbed or adhered on the surface of the large crystals. The emission decays of the washed crystals do not depend on the interrogated point (Figure 11C and Figure S9C). Therefore, the observed behavior in the unwashed crystals (peak at 425 nm, FWHM, and different lifetimes) are not due to intrinsic defects on the crystals. The fit of the decays shows a biexponential behavior with time constants of 500–580 ps (85–94%) and 2.4–3.0 ns (15–6%) (Table S7). To make an

easy comparison between the results of the unwashed and washed crystals, Table S8B shows a summary of the time constants and their contributions. The absence of the 4.5 ns component, which appeared in the unwashed crystals, leads us to suggest that the solvent has interpenetrated in the HOF network (probably in the H-bonds) by frustrating these connections, causing the lack of species having a H-bond character. This fact is also supported by numerous articles explaining that, during the crystallization of the HOFs, the solvent interpenetrates in the H-bonds, thus frustrating the right position of the molecular units to make the network.^{9,49,68–70}

To be able to study the anisotropy of the material, we carried out fluorescence confocal microscopy measurements on **Ex-*apo*** crystals, which show a high anisotropic emission behavior (Figures 10D and 11D). The emission anisotropy distribution displays one narrow band with the intensity maximum around 0.1. The extremely narrowed distribution anisotropy suggests a large orientation of the emitters inside the crystals. Previously, we have reported on other HOFs with different fundamental units, displaying a large anisotropic behavior.^{32,33,48}

Finally, comparing our previous report on HOF **T12-*apo*** with the present one (HOF **Ex-*apo***), we observed that an expansion of the core of the fundamental units, which leads to an increase in the pore size of the HOF, modifies the photobehavior. For **T12-*apo***, we have observed that the emission spectra of large crystals display a vibrational structure due to the rigidity of the network and a long fluorescence lifetime (22 ns). However, the emission spectrum of **Ex-*apo*** does not exhibit such a vibrational structure, and its longest fluorescence lifetime is 4.2 ns. These results can be explained by the higher network flexibility of **Ex-*apo*** compared to that of **T12-*apo***, as a result of the expansion in the fundamental units of the former one.

4. CONCLUSIONS

In this work, we have reported on studies of two phenylene-ethynylene macrocycles: **Ex-COOH** and **Ex-COOMe**. Theoretical calculations show that the **Ex-COOH** molecule could exhibit an ICT at S_1 and that different complexes can co-exist at the S_0 due to strong interactions between the acid groups and the DMF molecules. Experimentally, **Ex-COOMe** in DMF exists in one conformation, and upon excitation, we have observed emissions from the initially excited state (940 ps) and ICT species (2.02 ns) produced by an ICT reaction in 2.5 ps. For **Ex-COOH** in DMF, we observed emissions of different species, whose fluorescence lifetimes go from 400 ps to 5.95 ns. Moreover, the ICT reaction is faster in **Ex-COOH** (<200 fs) than in **Ex-COOMe**. The ns flash photolysis experiments on **Ex-COOH** indicate two different triplet states having lifetimes of 0.45 and 2 μ s. From the solid-state experiments, we observed that both excited materials show fluorescence lifetimes from 100 ps to 4.8 ns. Fluorescence microscopy experiments on HOF **Ex-*apo*** single crystals indicate that they do not exhibit a photobehavior dependent on the interrogated site, while their emission anisotropy shows that the emitters are well oriented in the crystals. We believe that the present findings will trigger more research in the family of shape-persistent phenylene-ethynylene macrocycles and related HOFs for potential applications in photonics.

■ ASSOCIATED CONTENT

SI ■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.0c01369>.

Optimized molecular structure of Ex-COOH interacting with six molecules of DMF (Scheme S1), the structures of the studied molecules similar to the ones of this report (Scheme S2), the diagram of the energy level of Nu-Ex and Ex-COOH in DMF (Figure S1), the absorption and emission spectra of Ex-COOH in DMF solutions with 0.1 M of NaOH (Figure S2), the excitation spectra of Ex-COOMe and Ex-COOH at different concentrations in DMF (Figure S3), the not normalized TRES of Ex-COOMe and Ex-COOH in DMF solutions (Figure S4), the ns- μ s transient absorption decays of Ex-COOH (Figure S5), the fs emission transient at a longer time window of Ex-COOMe and the concentrated sample of Ex-COOH in DMF solutions (Figure S6), FLIM, emission spectra, decays, and anisotropy of different crystals of Ex-*apo* unwashed (Figures S7 and S8), a fluorescence microscopy study of Ex-*apo* crystals washed with acetone (Figure S9), the data of the internuclear distance and the Mulliken charges of different electronic states of Nu-Ex and Ex-COOH (Tables S1–S4), the value of the relative energy stabilization of Ex-COOH interacting with DMF molecules (Table S5), the obtained data from the fits of the transient absorption decays of Ex-COOH in DMF solutions under air, oxygen, and nitrogen atmospheres (Table S6), and all the obtained time constants and pre-exponential factors used in the fit of the emission decays of Ex-*apo* single crystals using a fluorescence microscope (Tables S7 and S8) (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Ichiro Hisaki – Research Institute for Electronic Science, Hokkaido University, Sapporo, Hokkaido 001-0020, Japan; orcid.org/0000-0002-8170-5605; Email: hisaki@es.hokudai.ac.jp

Abderrazzak Douhal – Departamento de Química Física, Facultad de Ciencias Ambientales y Bioquímica, and INAMOL, Universidad de Castilla-La Mancha, 45071 Toledo, Spain; Email: abderrazzak.douhal@uclm.es

Authors

Eduardo Gomez – Departamento de Química Física, Facultad de Ciencias Ambientales y Bioquímica, and INAMOL, Universidad de Castilla-La Mancha, 45071 Toledo, Spain

Maria Rosaria di Nunzio – Departamento de Química Física, Facultad de Ciencias Ambientales y Bioquímica, and INAMOL, Universidad de Castilla-La Mancha, 45071 Toledo, Spain

Miquel Moreno – Universitat Autònoma de Barcelona, Bellaterra 08193, Barcelona, Spain

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/acs.jpcc.0c01369>

Author Contributions

I.H. designed and made the materials. M.M. performed the theoretical calculations and wrote the theoretical results. E.G. and A.D. designed and carried out the experiments, analyzed,

and discussed the theoretical and experimental results. E.G., M.R.d.N., and A.D. wrote the manuscript. All the authors have read the manuscript.

Notes

The authors declare no competing financial interest.

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