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Photophysical properties of hexapyrrolidine C_{60} adducts with T_h and D_3 symmetry: protonation of multiple basic sites

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Abstract

The effect of protonation on the absorption and emission properties of two isomeric hexapyrrolidine C_{60} adducts with T_h and D_3 symmetry has been studied. Results show that protonation does not modify substantially the interesting emissive properties reported in previous work for the neutral forms. The absorption and fluorescence spectra, as well as the fluorescence decay, are insensitive to protonation at any acid concentration for the D_3 isomer, while small changes are seen for the T_h isomer. For the latter, as the positive charge of the molecule increases the absorption spectrum shifts to lower wavelengths, the emission spectrum shifts to the red, and the fluorescence lifetime increases. The behavior of this isomer upon acid addition can be explained on the basis of a complex equilibrium between species having different degrees of protonation. Results show that the equilibration rates among the various species in the excited state are slower than the fluorescence decays, and consequently the measured decay is a weighted average decay of the individual species. The surprising difference in the behavior of the D_3 isomer was shown not to originate from significant differences in the basicity of the nitrogen atoms, but probably due to differences in the polarizability of the two π-systems. ©1999 Elsevier Science S.A. All rights reserved.

Keywords: Time-resolved luminescence; Fluorescence lifetime; Acid-base equilibrium; Fullerenes

1. Introduction

One of the strongest motivations for the functionalization of C_{60} comes from the rich photophysical and electrochemical properties expected by controlled manipulation of the conjugated fullerene core. Addition reactions that saturate two carbons at a time may expose a wide variety of interesting chromophores with condensed and linearly conjugated π-electron topologies possessing the unique curvature of the C_{60} surface.

We recently reported the highly selective synthesis and unusual photophysical properties of two hexapyrrolidine adducts of C_{60} with T_h and D_3 symmetries (compounds **1** and **2**, Fig. 1) [1]. Although both compounds are characterized by high intersystem crossing yields, we were pleased to discover that both hexaadducts have relatively high fluorescence yields as compared to other fullerenes [i.e., $\Phi_F(\mathbf{1}) = 0.02$ and $\Phi_F(\mathbf{2}) = 0.024$]. Unlike other C_{60} derivatives, the triplet states of **1** and **2** have a very slow thermal decay and deactivate at low temperatures (77 K) by emitting a remarkably long-lived phosphorescence (i.e., $\tau_T(\mathbf{1}) = 3.7$ and $\tau_T = 4.3$ s). The fluorescence of hexaadducts **1** and **2** occur in the 500–600 nm range and are about 10^2 times as intense as that of C_{60} [Φ_F $(C_{60}) = 3.2 \times 10^{-4}$], while their phosphorescence extends between ca. 620–750 nm, and their triplet lifetimes are remarkably 10^6 times as long as that of C_{60} [τ_T $(C_{60}) = 4 \times 10^{-5}$ s].

Aside from their synthetic potential for further architectural elaboration, one of the most interesting features of the structures of **1** and **2** comes from the possible interaction between the six nitrogen lone pairs and the fullerene π-electron system. From a photophysical point of view, it is known that C_{60} and most of its simpler derivatives possess electron affinities that make them excellent photoinduced electron acceptors towards amines. However, in analogy to known monopyrrolidine adducts [2–5], the excited states of **1** and **2** are not significantly quenched by intramolecular electron transfer as a result of the poor overlap between the pyrrolidine lone pairs and the fullerene π-electrons, and the fact that taking into account the distances involved in this system, a tertiary amine is not strong enough as a donor to overcome the barrier imposed by the large solvent reorga-

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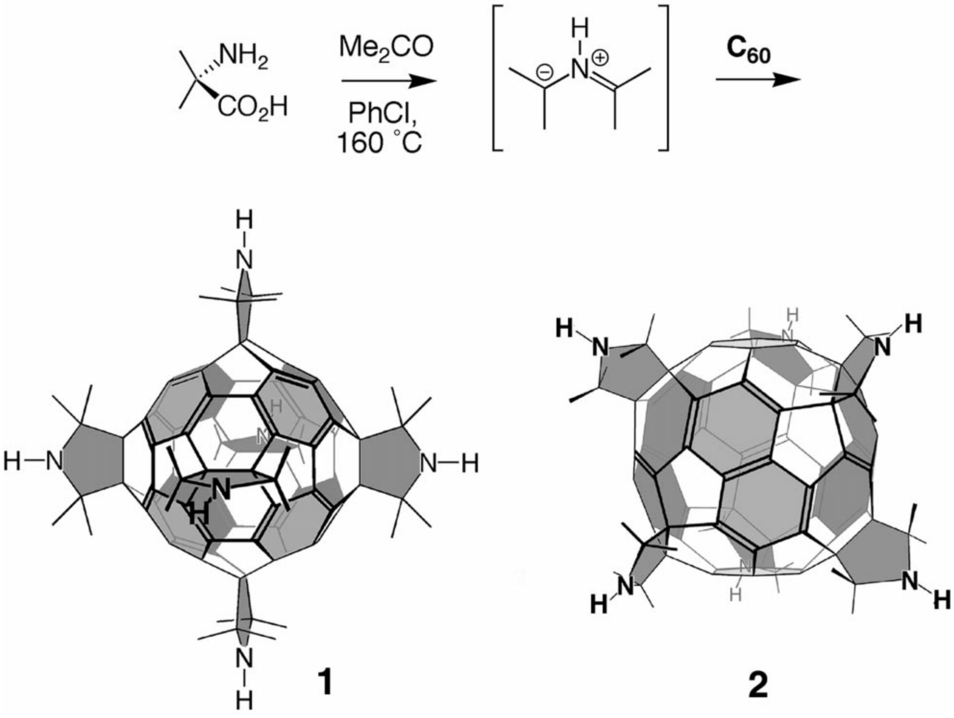


Fig. 1. Reaction scheme and structures of the T_h (**1**) and D_3 (**2**) hexapyrrolidine isomers.

nization. This quality may be important not only to have high emission yields, but also to maintain the photophysical properties of **1** and **2** intact when the nitrogen lone pairs are engaged in bonding.

Although the fluorescence quantum yields of **1** and **2** are modest by comparison to those of the most commonly used fluorescence dyes, we recently discovered that the T_h isomer can be used in the fabrication of white light emitting electroluminescent devices [6]. Since the ability to synthesize quaternary ammonium ions or metal ion complexes while maintaining the photophysical properties of hexaadducts **1** and **2** would be highly desirable, we report in this paper a systematic analysis of the effect of protonation on the photophysical properties of compounds **1** and **2**. We describe the effects of added acids on absorption, emission, and fluorescence lifetimes of both hexaamines. The results obtained for compounds **1** and **2** are significantly different from each other. While compound **1** responds to added acid in a complex manner, no changes were observed for compound **2** at any acid concentration, either in organic or in aqueous media. The results for compound **1** are interpreted in terms of multiple concurrent acid-base equilibria where the photophysical properties of neutral, low and high protonation states may be distinguishable. The remarkable lack of acid sensitivity of **2** spans from TFA in acetonitrile to concentrated hydrochloric acid. We suggest that the different sensitivities of **1** and **2** to acids probably reflect differences in polarizability of the two π-systems as they respond to the nearby quaternary ammonium ion point charges.

2. Experimental section

2.1. Materials

The synthesis of hexaadducts **1** and **2** was reported in our previous paper [1]. Acetonitrile (Fisher, HPLC grade) was dried and degassed prior to use. Trifluoroacetic acid (TFA) and deuterated trifluoroacetic acid (TFA-d) were purchased from Aldrich and manipulated under argon.

2.2. Measurements

Absorption spectra were obtained with a Hewlett Packard 8453 spectrophotometer. Fluorescence spectra were recorded with a Spex-FluorologII spectrofluorimeter and corrected for non-linear instrumental response. Fluorescence decays were measured with a time-correlated single photon counting fluorimeter (Edinburgh Instruments, Model FL900CDT) equipped with a pulsed H_2 discharge lamp operating at 0.4 bar. When necessary, the fluorescence intensity was attenuated to obtain an average number of detected fluorescence photons lower than 0.5% of the excitation source repetition rate (40 kHz). The decay, $D(t)$, was assumed to be well represented by the sum of two exponential terms,

$$D(t) = C + A_1 \exp\left[\frac{-(t+\delta t)}{\tau_1}\right] + A_2 \exp\left[\frac{-(t+\delta t)}{\tau_2}\right] \quad (1)$$

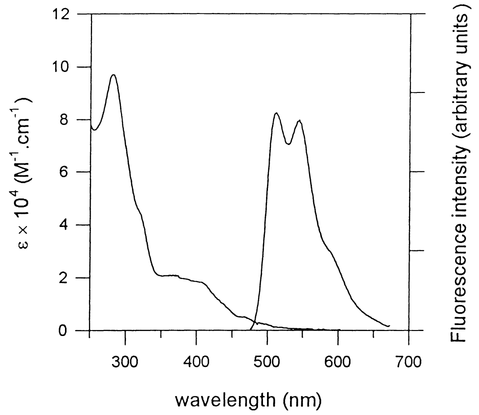


Fig. 2. Absorption and fluorescence emission spectra of the D_3 hexaadduct **2**.

where the temporal shift, δt, was used to compensate for small positioning errors in the leading edge of the decay caused mainly by instrument wavelength effects present in the lamp profile. The experimentally measured luminescent emission, $F(t)$, was deconvoluted from the instrumental response, $I(t)$, to obtain $D(t)$. The instrumental response was measured using a LUDOX suspension as a scattering sample, setting both monochromators at the emission wavelength of the sample. The goodness of each fit was evaluated from the shape and magnitude of the weighted residuals, $R(t)$. All decays were measured until 1000 counts were collected at the peak. It was verified that the parameters in Eq. (1) did not change within experimental error upon collection of counts beyond this number.

3. Results

Fig. 2 shows the absorption and fluorescence spectra of a 10^{-5} M solution of the D_3 isomer (**2**) in acetonitrile. A fluorescence quantum yield of 0.02 was measured previously [1] and its decay was adequately fitted by a monoexponential with a lifetime of 3.2 ± 0.2 ns. No appreciable changes were observed in the shape of the absorption and emission spectra, the fluorescence quantum yield, or the lifetime, upon addition of 1% TFA in acetonitrile. Remarkably, no changes in emission spectrum or lifetime were observed when **2** was dissolved in concentrated (12 M) hydrochloric acid. In contrast, the photophysical properties of the T_h hexaadduct **1** varied appreciably upon the addition of TFA. Fig. 3 shows the UV-Vis spectra of a 4×10^{-6} M solution of **1** in acetonitrile, and in the presence of increasing amounts of TFA. Spectra taken with concentrations of TFA lower than 1.6×10^{-5} M (not shown in Fig. 3 for clarity) are almost coincidental with the spectrum of the neutral form (Curve a). The corrected fluorescence spectra of the same samples normalized by the absorbance at the excitation wavelength (fixed at 300 nm) are shown in Fig. 4. Changes in excitation wavelength between 300–370 nm have a pronounced effect on the emission spectrum of **1**. This is illustrated in Fig. 5 by measurements with a sample containing 5×10^{-3} M TFA. The fluorescence quantum yield of the neutral form in acetonitrile increases from 0.024 to as much as 0.043 in the presence of 1% (V/V) TFA [1]. The fluorescence decay of solutions of **1** in the absence of acid was monoexponential with a lifetime of 3.6 ± 0.2 ns. After addition of TFA, it was always necessary to consider a second exponential term to adequately fit the emission decays. Fig. 6 shows the decay of the neutral solution and a solution 4×10^{-6} M in **1** and 1.0 M in TFA. All the decays were independent of temperature within the range investigated (ca. 25–60°C) and did not change within experimental error upon replacement of TFA by TFA-d.

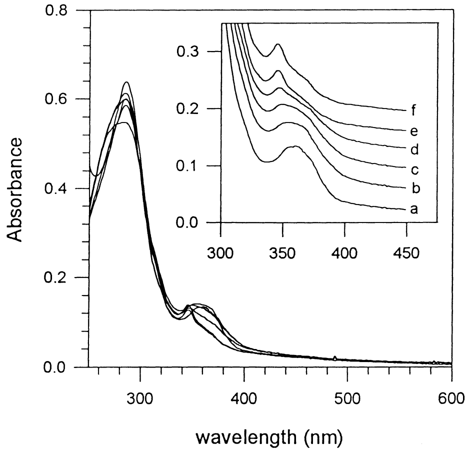


Fig. 3. Absorption spectra of a 4×10^{-6} M solution of the T_h hexaadduct **1** in acetonitrile (a), and upon addition of TFA: (b) 1.6×10^{-5} M, (c) 3.5×10^{-5} M, (d) 1.5×10^{-4} M, (e) 4.6×10^{-3} M, and (f) 0.05 M.

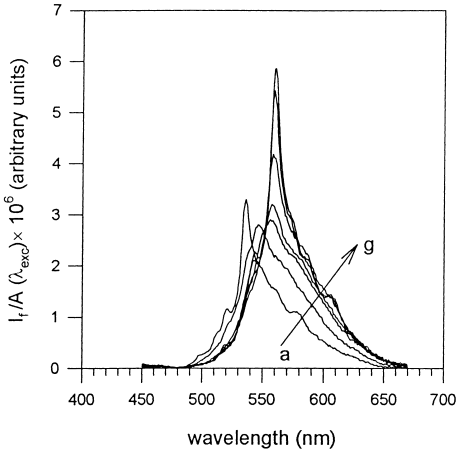


Fig. 4. Fluorescence emission spectra of a 4×10^{-6} M solution of the T_h hexaadduct **1** in acetonitrile (a), and upon addition of TFA: (b) 4×10^{-6} M , (c) 1.6×10^{-5} M, (d) 1 3.5×10^{-5} M, (e) 1.5×10^{-4} M, (f) 4.6×10^{-3} M, and (g) 0.05 M.

Table 1 shows all the relevant fitting parameters of decays measured with different concentrations of TFA and at different emission wavelengths. The concentration of **1** was 4×10^{-6} M and the excitation wavelength 300 nm in all cases.

Table 1
Relevant fitting parameters of the decays of compound **1** with various concentrations of TFA

TFA concentration (emission wavelength [nm])	τ_1(ns)	τ_2(ns)	$100 \times A2/(A2+A1)^a$ %
No TFA (550)	3.6 ± 0.2	–[b]	–[b]
8×10^{-7} M (550)	2.5 ± 1	6.9 ± 0.2	77
4×10^{-6} M (550)	2.5 ± 1	9.1 ± 0.2	84
4×10^{-6} M (510)	2.5 ± 1	8.9 ± 0.5	57
4×10^{-6} M (570)	2.5 ± 1	9.0 ± 0.5	80
4×10^{-5} M (550)	2.5 ± 1	10.6 ± 0.2	68
0.011 M (550)	2.5 ± 1	12.3 ± 0.2	86
0.11 M (550)	2.5 ± 1	12.8 ± 0.2	83
1 M (550)	2.5 ± 1	13.2 ± 0.2	74

[a] This value represents the relative weight of the longest time.
[b] The decay was monoexponential.

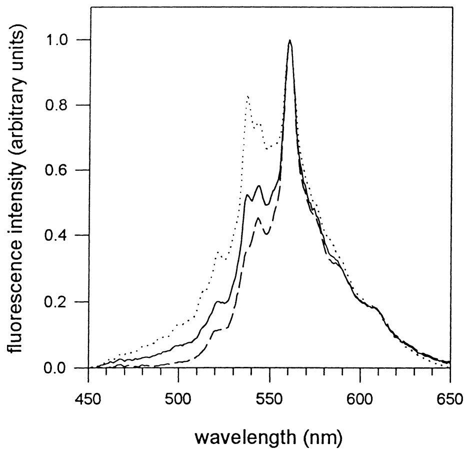


Fig. 5. Fluorescence emission spectra of a 4×10^{-6} M solution of the T_h hexaadduct **1** in acetonitrile with 5×10^{-3} M TFA obtained with excitation at: (------) 300 nm, (——) 350 nm, and (·········) 370 nm.

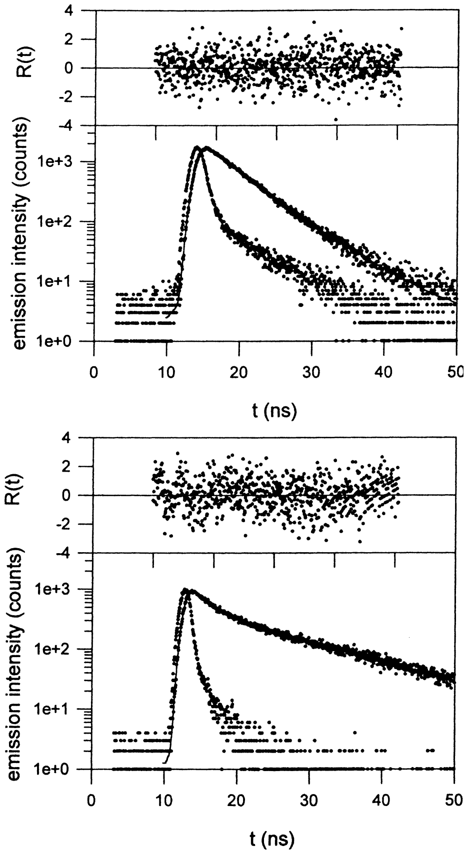


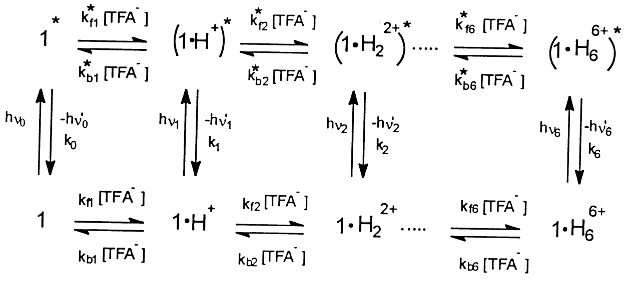
Fig. 6. Instrumental responses, decay traces, fitting curves and residuals obtained with a 4×10^{-6} M solution of the T_h hexaadduct **1** in acetonitrile (top) and in the presence of 1.0 M TFA (bottom). Residuals values are in standard deviation units.

The large error for the shorter component arises from the fact that the portion of the decay corresponding to this time is superimposed to the instrumental response and the corresponding pre-exponential factor is usually small. The error was estimated by evaluating the quality of fit with this time fixed at different values and noting when it changed significantly: in all cases the quality of the fit remained unchanged by increasing the short component up to ca. 3.7 ns. The value of the longest time was not sensitive within experimental error to this change. Although the two lifetimes were independent of emission wavelength, changes in the two pre-exponentials were observed.

4. Discussion

Despite the relatively different π-systems, Compounds **1** and **2** have similar excitation energies and singlet and triplet state photophysics. The lack of intramolecular electron transfer in the excited states of **1** and **2** was previously documented by the small or negligible changes in their fluorescence spectra, quantum yields and lifetimes in solvents of different polarity [1]. The small or absent photophysical response of **1** and **2** towards the addition of acids, also confirms the lack of electron transfer quenching. Possible concerns regarding the protonation of **2**, which could in principle be an unusually weak base, are not supported by the solubilization of the quaternary ammonium salt in aqueous solutions.

Regarding the effects of protonation on the photophysics of compound **1**, the results in Figs. 2 and 3 reveal that the effect of added TFA on the absorption and fluorescence spectra are not identical. The different sensitivities of absorption



Scheme 1.

and emission to the addition of TFA may be interpreted in terms of three general models: (a) the extent of protonation is different in the ground and excited states, (b) protonation has different effects on the transitions responsible for the observed changes in absorption and emission, or (c) a combination of the two. A tentative distinction to generate a working model can be made by noting that as little as 1 equivalent of TFA causes a nearly quantitative change in fluorescence lifetimes (see Table 1) at concentrations ($<10^{-4}$ M) where diffusion controlled rates would preclude equilibration of the excited states within their nanosecond lifetimes. This simple analysis suggests that monoprotonation must be nearly complete in the ground state with only one equivalent of the acid, despite the lack of a change in the UV absorption spectrum. In fact, although TFA is a relatively week acid in acetonitrile (pKa = 14 [7]), the equilibrium constant for the reaction

$$\mathrm{TFA} + (\mathrm{MeCN}) \rightleftarrows \mathrm{TFA}^{-}\,(\mathrm{MeCN}) + 1\mathrm{H}^{+}\,(\mathrm{MeCN}) \qquad (2)$$

can be estimated to be about 4×10^4. This comes from the fact that pK(MeCN)-pK(H_2O) is 14 for carboxylic acids, and 7.3 for the dissociation of quaternary ammonium ions [7]. At a first approximation, the dissociation constant of the **1**·$\mathbf{H}^+$ ion can be assumed to be similar to the corresponding value for the pyrrolidinium ion[2] which has a pKa = 11.27 in water [8]. The fact that the absorption spectrum of samples containing up to four times more TFA than **1** is almost identical to the spectrum of the neutral solution indicates that the absorption spectrum of species with low degree of protonation is very similar to the spectrum of the neutral form. Only when the concentration of TFA is about ten times as large as that of **1** does the absorption spectrum shift to lower wavelengths. The lack of an isosbestic point in Fig. 3 indicates complexities due to the existence of more than one equilibrium step. As shown in Scheme 1, k_0, $k_1 \ldots k_6$ represent the rate constant for the decay of each species, and $k_{\mathrm{f},i}$, $k_{\mathrm{b},i}$, $k^*_{\mathrm{f},i}$, and $k^*_{\mathrm{b},i}$ represent the forward and backward rate constant of the ith step in the ground and excited (*) state, respectively. As the positive charge around the T_h adduct increases, the equilibrium constant for each reaction step (given by $K_i = k_{\mathrm{f},i}/k_{\mathrm{b},i}$) is expected to decrease.

The presence of multiple species suggested by the UV spectrum could be readily confirmed with fluorescence measurements which revealed the presence of several species with emission maxima shifting to the red as the degree of protonation increases. An increase in the Stokes shift with increasing protonation is probably a consequence of the better solvent stabilization of excited states with a greater charge. Interestingly, the fluorescence quantum yield increases only at the highest acid concentrations. While equilibrium for the monoprotonated species appears not to occur in the excited state, this may not be the case at high concentrations of TFA. As indicated in Scheme 1, the solution may contain several protonated species with concentrations that depend on the concentration of TFA and their equilibrium constants. These species will absorb according to their concentration and extinction coefficients and will have their characteristic fluorescence yields. As before, three different situations can be distinguished depending on the relative values of the forward and backward reactions of each equilibrium in the excited state ($k^*_{\mathrm{f},i}$, $k^*_{\mathrm{b},i}$) and the decay rate of each species ($k_{\mathrm{d},i}$). In one limit, emission reflects the heterogeneity of a ‘frozen’ equilibrium, where the concentration of each species is the same in the excited state and in the ground state. The alternative occurs from a fully equilibrated system where the concentration of each species is dictated by the excited state equilibrium constants. In the most complex case, emission occurs when equilibrium is not completely achieved and the concentration of each species in the excited state is not the same as in the ground state.

The fact that the emission spectra of solutions containing 10^{-3} M TFA depend strongly on the excitation wavelength (see Fig. 5) indicates that the solution contains more than one species with different absorption and emission properties, and that the rate of the equilibrium is slow compared with the lifetime of the excited states. When the solution is excited at short wavelengths, where the more highly protonated species absorb, the emission arises predominantly from the protonated species which emit with a maximum around 560 nm. As the excitation wavelength is shifted to longer values, species with low degree of protonation are selectively excited and the intensity of the band around 535 nm increases relative to the band at 560 nm. In general, the rate of the forward reaction of a carboxylic acid and a base in water tends to be ca. $2 \times 10^9\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}$ when the pKa of the acid is at least two orders of magnitude lower than the pKa of the protonated base [7]. If one assumes a similar rate in acetonitrile[3], an equilibrium constant of

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[2] Prato reported recently that C_{60} causes a decrease of almost six orders of magnitude in the basicity of a pyrrolidine nitrogen in a C_{60} monoadduct (see [11]). This was attributed to the strong electron-withdrawing properties of the fullerene, which diminish the availability of the nitrogen lone pair. While one may expect a weaker effect in the T_h hexaadduct due to the higher localization of its π-system, the qualitative conclusions proposed here do not depend on the precise basicity value.

[3] Taking into account the relative viscosities of the two solvents, the forward rate constant in acetonitrile can be as 2.5 times larger than the corresponding value in water, but this difference is not significant for the current estimation.

4×10^4 for the first protonation gives an estimate of about $5 \times 10^4\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ for the dissociation rate. Considering the concentrations of TFA and **1**, it is clear that acid base chemistry would be too slow to compete with excited state decay in the nanosecond time-scale. This conclusion is also supported by the fact that the experimental decays are independent of temperature and do not show an isotope effect, even at relatively high concentrations of TFA. A change in temperature or the replacement of hydrogen by deuterium in the carboxylic acid would be expected to produce a change in $k^*_{\mathrm{f},i}$ and $k^*_{\mathrm{b},i}$ which would affect the observed decay only if the acid-base reaction competes with the excited state decay (see [9] and [10] for a detailed discussion on how the change in $k^*_{\mathrm{f},i}$, and $k^*_{\mathrm{b},i}$ would affect the decay rates).

Taking into account the above considerations, the acid-base reaction is not expected to compete with the excited state decay, and each measured decay is the sum of monoexponential terms representing the individual decay of each species. Each pre-exponential factor will depend on the concentration of each species as well as on their absorption and emission properties. The fact that all decays were satisfactorily fitted by a biexponential equation indicates that the system is always well represented in average by two species having significantly different lifetimes. For each decay, the smallest time is very similar to the time measured without TFA, indicating that the species with low degree of protonation have a similar lifetime to the neutral species. Even when the TFA concentration is high, a significant concentration of species with small degree of protonation remains in solution due to the fact that the equilibrium constant is expected to decrease considerably as the charge of the molecule increases. These results are consistent with the observations of the dependence of the emission spectrum on the excitation wavelength described above.

As the concentration of TFA increases, the contribution from the longer-lived component also increases, clearly indicating that species with higher degree of protonation have longer lifetimes. The increase in the lifetime of the protonated species compared with the neutral species may be responsible for the observed increase in quantum yield. The effect of changing the emission wavelength can be analyzed by comparing rows 3–5 in Table 1. While changes were observed on the relative contribution of each component, the two lifetimes remain unchanged. Since these measurements were performed at constant excitation wavelength and constant T_h and TFA concentrations, the change in the pre-exponential factors reflects only the difference in the emission properties of species with different degrees of protonation. The relative contribution of the shortest-lived component increases the emission wavelength shifts to the blue, where the species with lower degrees of protonation emit more efficiently. A comparison of the pre-exponential factors of experiments performed with different amounts of TFA is not straightforward since the relative weight of each time depends not only on the emission profile (including the emission quantum yield) of each species, but also on the relative concentration and the extinction coefficient of each species at that excitation wavelength.

5. Conclusions

In this paper we studied the effect of protonation on the photophysical properties of two isomeric hexapyrrolidine C_{60} hexaadducts. Both the kinetic and spectroscopic properties of the two isomers showed minor changes upon acid addition, indicating that intramolecular electron transfer does not play a substantial role in the photophysics of these compounds. For the T_h isomer **1**, acid addition not only does not quench fluorescence but increases the fluorescence quantum yield by a factor of ca. 2, probably due to the longer singlet lifetime of the protonated species as compared with the neutral form. In this way, we have shown that protonation of the pyrrolidine nitrogen atoms preserves the interesting emissive properties of the neutral form reported in a previous paper [1].

The dependence upon acid addition of the kinetic and spectroscopic properties of the T_h isomer can be explained on the basis of a multiple acid-base equilibrium between species having different degrees of protonation. Results show that since the equilibration rate between these species is slow compared with the decay rate, there is no exchange between species in the excited state. In this way, all measured decays can be then interpreted as a weighted average of the individual decays.

The different behavior of the D_3 isomer was shown not to be due to a lower basicity of the pyrrolidine nitrogens, since the photophysical properties of this isomer remained unchanged even in aqueous concentrated acid, where the neutral form is insoluble. We suggest that the difference in the behavior of the two isomers may be related to differences in the polarizability of the two π-systems, which would respond differently to the positive charges located at the nitrogen atoms.

Acknowledgements

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