



Hidden blue emission in [60]fullerene stemming from weak π - π aggregation

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ABSTRACT

The unusual UV/blue-green fluorescence of [60]fullerene at micromolar concentrations in ethyl acetate is investigated using steady-state and time-resolved fluorescence techniques. This broad emission exhibits longer lifetimes (≈ 10 ns) than the well-known weak red fluorescence typically associated with C_{60} (≈ 1 ns). The relative intensity of the blue and red emissions is influenced by several factors, including C_{60} concentration, sonication, solvent polarity, the presence of additives (e.g., inert gases or oxygen), and excitation wavelength. Evidence from time-resolved fluorescence anisotropy and computational studies suggests that the unconventional emission originates from the formation of ~ 2 nm-sized fluorophores due to weak intermolecular π - π van der Waals interactions, which become ineffective at concentrations below $2 \mu\text{M}$, this concentration being the estimated value for the solubility of C_{60} in ethyl acetate. Interestingly, since the intense and long-lived unconventional emission of aggregated C_{60} is sensitive to molecular oxygen or solvent polarity, a novel functionality for the singlet excited state of this emblematic molecule in its aggregated state as a luminophore, a fluorescent probe or a photosensitizer has been unveiled.

1. Introduction

Since the discovery of fullerenes by Kroto, Smalley and Curl in 1985 (Nobel Prize in Chemistry in 1996) [1], and the subsequent detailed characterization of their properties [2,3], the scientific community has been dedicated for decades to developing successful technological applications of fullerenes and their derivatives. Many of these advances are related to the particular photophysical properties of [60]fullerene, including a wide range of uses in photochemistry and photosensitization [4], photocatalysis [5], photovoltaics [6], (photo)biology and biomedicine [7,8], energy conversion and storage [9], as well as in new

materials for different novel applications [10].

Harry Kroto reported the absorption spectrum of C_{60} [11], describing strong absorption bands in the UV region as well as weak absorption peaks or band shoulders in the visible region, with absorption coefficients about $1000 \text{ M}^{-1} \text{ cm}^{-1}$ or lower and substantial solvent effects [12]. Regarding the fluorescence [13], the very weak red emission of C_{60} shows some structure with peaks at 688 and 718 nm (0–0 vertical transition $S_1 \rightarrow S_0$ at 620 nm or 2.00 eV) [14], a very low fluorescence quantum yield (around 1.5×10^{-4} in benzene-like aromatic solvents) and a short emission lifetime of the excited singlet ($\tau_S \approx 1.2$ ns) [14]. On the other hand, intersystem crossing from S_1 to T_1 (located at 1.57 eV)

This work is dedicated to Prof. Fred Wudl on the occasion of his 85th birthday.

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occurs very efficiently in C_{60} (triplet quantum yield, $\Phi_T \approx 1$), with a long-lived triplet excited state ($\tau_T \approx 250 \mu s$) [14].

However, although the photophysics of C_{60} and its derivatives has been studied in detail during the 1990's decade and by now seems to be clear, an intriguing question persists regarding the sporadically observed presence of an additional emission band in the blue or yellow-green spectral region. This phenomenon, initially detected in *n*-hexane at room temperature since the early days of C_{60} fluorescence characterization [15], has remained largely unstudied in detail. Consequently, this secondary emission remains an enigma, as it has not yet been the subject of a comprehensive description regarding C_{60} photophysics.

About one decade later, secondary emission bands of C_{60} (with peaks around 440 or 575 nm) were detected in several organic solvents, including DMSO and pyridine (where C_{60} solubility is low) but not in carbon disulfide or toluene solvents (where C_{60} shows higher solubility) [16]. The case of C_{60} solutions in pyridine was further studied, since two emission bands were observed in this solvent (ca. 440 and 575 nm) besides the typical C_{60} fluorescence band around 700 nm [17]. The new emissions were initially ascribed to strong interactions between solvent molecules and C_{60} , resulting in the formation of partial charge-transfer adducts formed by electron donating solvents and [60]fullerene as an effective electron acceptor, causing an important distortion of the molecular symmetry of C_{60} , relaxation of selection rules, and appearance of new and strong emission bands [16,17]. Simultaneously, single emission bands with enhanced fluorescence were observed in the 550 nm region in pearl-necklace polymers composed of C_{60} acceptors and aromatic diamine donors. The enhanced fluorescence was attributed to partial charge-transfer interactions between the aromatic amide moiety and the C_{60} units along the intramolecular chain [18].

Later, and surprisingly, two partly contradictory reports by the same authors in 2006 revisited the fluorescence of C_{60} solutions in pyridine and described, on the one hand, that the three fluorescence bands of C_{60} , centered at 440, 575 and 700 nm, could be observed in supersaturated C_{60} -pyridine solution. The fluorescence peak centered at 440 nm was attributed to C_{60} molecules dissolved in the C_{60} -pyridine solution, while the fluorescence bands centered at 575 and 700 nm were ascribed to undissolved C_{60} [19]. On the other hand, in a second work, based on fluorescence and *in-situ* transmission electron microscopy measurements of C_{60} -pyridine and C_{60} -toluene supersaturated solutions, with different settling times at room temperature, they ascribed the peak centered at 440 nm to solvated C_{60} nanoparticles, the yellow-green fluorescence band located at 575 nm to C_{60} lace-like clusters with unsolvated [60] fullerene molecules, and the salmon-pink fluorescence band around 700 nm to large C_{60} microaggregates in solution [20]. Hence, this second study neglected the monomolecular red emission of [60]fullerene and supported the early idea by Kaneto et al. [21], according to which the C_{60} molecule in solution is not isolated, but assembled by forming clusters composed of several rapidly rotating and weakly interacting [60]fullerene units [22], which do not induce shifts of absorption or emission peaks compared to those observed in solution (referred to the fluorescence band at ca. 700 nm). Therefore, C_{60} molecules in solutions would actually be in the form of dispersed nanoparticles stabilized in suspension due to charge-transfer interactions with solvent molecules that cannot easily aggregate further because of the repulsion between the solvent cages.

More recent studies by these authors insisted on the aggregation of C_{60} molecules in different solvents or their mixtures to explain the fluorescence emission colors of the [60]fullerene bands centered at 440, 575 and 700 nm as a function of the relative size of the formed C_{60} nano-/micro-particles [23–25]. Without considering the distinct justifications provided, other works by different authors have recently reported similar additional emission bands, mainly in the blue spectral region, for [60]fullerene [26,27], or [60]fulleropyrrolidines [28], dissolved in benzene, toluene, xylene, *n*-hexane or trichloroethylene at sample concentrations well below the solubility limit of C_{60} in these solvents. Furthermore, it should be mentioned that, in these reports, the

experimental procedures carried out have taken into account careful consideration or correction for the solvent emission background, and the presence of disturbing Rayleigh and Raman bands, given the low fluorescence quantum yield of C_{60} [26,27].

Therefore, arguments concerning the confident assignment of [60] fullerene emissions in the region of ca. 700 nm or lower, due to solvated individual C_{60} molecules or C_{60} nanoparticles (C_{60})_n, must always bear in mind aspects such as the experimental setup (acquisition parameters, optical filters used and spectral corrections), the limited solubility of [60]fullerene (generally below 1–10 mM in common organic solvents) [29–31], and the specific non-monotonic C_{60} solubility behavior with temperature in some solvents [32–34], as well as the dissolution dynamics (where charge-transfer interactions can play a role) in connection with the sample preparation method [35–37]. In particular, since the specific surface energy of interactions between fullerene units with each other or with the solvent molecules are very close in magnitude [38], fullerenes in solution often tend to form aggregates, and factors such as the polarity of the solvent determine the eventual aggregation of the fullerenes (requiring threshold solvent dielectric constants greater than 12–14 for C_{60} and 27–31 for C_{70} , due to their different polarizabilities) [39]. For instance, unfunctionalized C_{60} dissolves best in apolar solvents such as toluene, chlorobenzene or carbon disulfide, but it still tends to slowly aggregate in solution (e.g. reversibly in benzene, but irreversibly in water) [40–43]. Likewise, in the case of C_{70} solutions in toluene-acetonitrile mixtures, a new excitation wavelength-dependent fluorescence band was observed at ≈ 590 nm (λ_{exc} 500 nm) when acetonitrile % was >70%, which was tentatively assigned to the Raman scattering peak due to the formation of aggregates [39].

Thus, although experimental results and theoretical calculations clearly attribute the excitation wavelength independent fluorescence band (peaking in the 680–740 nm interval) to individual C_{60} molecules [13,44,45], and the study of individual C_{60} molecules excited by local electron tunneling [46,47] has allowed the acquisition of the fluorescence and phosphorescence spectra of single C_{60} molecules (describing emission bands in the 700–750 nm region that adequately match the calculated fluorescence spectra of molecular [60]fullerene); the fact that fullerenes can form aggregates even at concentrations far below saturation in organic solvents [48], suggest that aggregation is a very important phenomenon that must be taken into account when interpreting the photophysics, not only of fullerenes but also of other carbon nanostructures such as carbon dots or molecular nanographenes [49, 50].

The aim of this research is to gain insights on the photophysics of [60]fullerene aggregates in solution, using ethyl acetate as a solvent with low dielectric constant (≈ 6.0 at 25 °C) where, however, C_{60} solubility is low and, to the best of our knowledge, still unknown. We have focused our work on the high dilution regime dominated by unimolecular deactivation processes where, besides the interactions with solvent molecules, intermolecular π -type interactions could still exist between C_{60} molecules. These intermolecular C_{60} - C_{60} interactions could in turn smoothly modulate the photophysics of [60]fullerene due to restricted mobility and dissimilar solvent accessibility with respect to the isolated C_{60} molecule [51], opening new avenues for aggregated C_{60} as a singlet exciton luminophore, photosensitizer or molecular probe. Therefore, this study on the changes in the photophysical properties of C_{60} in an organic solvent in which C_{60} shows limited solubility could shed light on the potential conditions for the appearance of additional emission bands in the fluorescence spectra of soluble [60]fullerene nanoaggregates that, under certain experimental conditions, could overcome one of the fundamental laws of photochemistry, Kasha's rule [52,53]. In this context, the role of molecular aggregation in shaping the excited-state properties of C_{60} , particularly through weak, non-covalent interactions, deserves closer examination and is a key part of this work.

2. Methods

2.1. Photophysical characterization

UV-vis absorption spectra were recorded in a single-beam Varian Cary 50 spectrophotometer, using quartz cells with 1 cm optical path length. For the characterization of the UV-vis spectrum, commercial [60]fullerene was purchased from Sigma-Aldrich. C₆₀ was dissolved in organic solvents of HPLC grade: ethyl acetate (Scharlau) and toluene (Scharlau). Two sets of C₆₀ samples in ethyl acetate were prepared from two different stocks (Sample 1, saturated, 50.0 μM, and Sample 2, supersaturated, 69.4 μM). The stock samples and their corresponding dilutions were used to perform this study. Correction for light scattering has been carried out with Fluortools software [54], following the methodology described elsewhere [51,55].

Fluorescence spectra were recorded using a FluoTime 300 time-correlated single photon counting (TCSPC) spectrofluorometer (PicoQuant, equipped with a 300 W Xe-lamp as a steady state excitation system with a spectral range from 250 nm to 2600 nm, a Peltier cooled photomultiplier tube (PMT, PMA-C 192-M type, 230–920 nm), and EasyTau 2 fluorescence spectrometer control and data analysis software, that allowed preliminary optimization of spectra and fluorescence decays acquisition parameters with the Wizard mode).

Acquisition parameters of the fluorescence excitation and emission spectra were optimized and applied to all samples. This optimization involves corrections by solvent background signal and corrections affecting the acquired spectrum due to the spectral shape of the excitation source or the response of the photomultiplier tube, for the excitation and emission spectra, respectively. Excitation/emission slits were 10/1, and the spectra were acquired with an integration time of 0.5 s. The absorbance of all samples studied by fluorescence spectroscopy is always less than 0.2 at the excitation wavelength (λ_{exc}) to achieve a compromise that avoids inner filter effect artifacts that cause distortion of the UV edge of the blue emission bands but allows sufficient emission signal to be obtained for fluorescence detection in the red spectral region, where C₆₀ emission is very weak. Acquisition of all the fluorescence spectra was performed by setting appropriate long-pass filters with cut-on wavelengths of either 395 or 435 nm in the emission path, in order to remove Rayleigh scattering light from the excitation source. These filters eliminate not only scattered excitation light, but also part of the fluorescence emission in the corresponding UV or blue region, respectively, yet still allow detection of the fluorescence signal in the UV-blue region of the spectrum. Smoothed spectra were obtained applying a Savitzky-Golay algorithm (30 points and second order polynomial) to raw data.

Fluorescence lifetimes were determined by TCSPC using a FluoTime 300 system (PicoQuant). Excitation with the FluoTime 300 apparatus was achieved by a diode laser head emitting at 373 nm (LDH-P-C-375, pulse duration <90 ps, supplying collimated picosecond laser pulses) and the emitted photons were detected keeping the count rate below 1% (PMA-C 192-M PMT and TimeHarp 260 PICO Single TCSPC PC plugin board for PCIe bus-independent channels with 25 ps temporal resolution). Data were analyzed by the PicoQuant's FluoFit software using the light scattering correction mode.

Fluorescence spectra and emission lifetimes under inert atmosphere were measured with solvent saturated Ar-purged solutions (Ar 99.998 %, Carbueros Metálicos).

Time-resolved fluorescence anisotropy experiments were carried out with the FluoTime 300 apparatus equipped with an automated polariser in the emission arm (15 mm Glan Thompson prism, UV grade with wavelength range 220–1900 nm). These experiments allowed the estimation of the average hydrodynamic volume (V) of the fluorophore moieties by acquisition of the emission decays with parallel and perpendicular polarizations relative to the polarization of the excitation laser (373 nm) using a linear polarizer installed in the light detection path. Equation (1) was used [56]:

$$V = \frac{k_B T \tau_{\text{rot}}}{\eta} \quad (1)$$

where k_B is the Boltzmann constant (J·K⁻¹), T the absolute temperature (K), τ_{rot} the average rotation time (s), and η is the dynamic viscosity of the solution (Pa·s) at 25 °C [57]. From the estimated spherical hydrodynamic volume, the radii and diameters of the fluorophores were directly determined.

2.2. Computational methods

2.2.1. Semiempirical calculations

C₆₀ structure was fully optimized using Gaussian 16 (Revision A.03) [58], at the semi-empirical PM7 level of theory [59]. All atoms were assigned to zero partial charge, consistent with treating C₆₀ as an uncharged (neutral) species. Absorption spectra of the monomer, tetramer, and nonamer were calculated using the ZINDO method on structures extracted from molecular dynamics trajectories [60]. Calculations were performed for 250 states of the monomer, 250 states of the tetramer and 400 states of the nonamer, corresponding to energy ranges of 2.12–5.42 eV, 2.00–3.67 eV and 2.08–3.45 eV, respectively. To account for solvation effects, critical for accurate UV-vis absorption predictions, we used the IEF-PCM implicit solvent model with the dielectric constant $\epsilon = 6.86$ for ethyl acetate [61]. A complete dataset of the computational results is available from the ioChem-BD repository at <https://doi.org/10.19061/iochem-bd-2-84> [62,63].

2.2.2. Density functional theory (DFT) calculations

The ground and excited states of the tetramer were calculated using Gaussian 16 (Revision A.03), employing the GGA functional PBE [64, 65], and the def2-SVP basis set for carbon atoms [66,67]. Solvent effects were included in the same manner as in the semiempirical calculations. The excited state (S_n) corresponds to the most probable electronic transition within the blue emission range (2.7–2.8 eV), computed using the *alter* keyword. To ensure that the electronic transition involved the selected molecular orbitals and did not undergo reorganization, the SCF convergence threshold was relaxed to 10⁻⁵.

2.2.3. Molecular dynamics (MD) simulations

To investigate the behavior and aggregation of C₆₀ in ethyl acetate, we performed all-atom molecular dynamics simulations with explicit solvent using GROMACS 2019.3 [68,69]. All fullerene molecules were treated as rigid bodies (a choice justified by the clear separation of time scales between the high-frequency, small-amplitude intramolecular vibrations of the sp² carbon cage and the low-frequency translational and rotational motions that govern aggregation). In the temperature range studied, any small elastic deformations of the cage contribute only marginally to the intermolecular potential of mean force (PMF) and therefore do not affect key observables of self-assembly (radial distribution functions, cluster-size distributions). The same rigid-body approach has been successfully applied and validated in other intrinsically rigid, highly symmetric systems such as polyoxometalates (where it accurately reproduces aggregation thermodynamics, structure factors, and phase behavior) [70–72]. This body of evidence supports the transferability of the rigid-body approximation to fullerenes in the present context.

The total potential energy of the system was represented as the sum of bonded terms (bond stretching, angle bending, and dihedral torsions) and non-bonded terms. Non-bonded interactions were described by pairwise additive 1-6-12 Lennard-Jones and Coulombic potentials, with exclusions for atom pairs separated by three or fewer covalent bonds. Non-bonded parameters for C₆₀ were taken from Smith et al. [73], who optimized them to reproduce experimentally measured C₆₀ crystal properties; the ethyl acetate solvent was modeled with the all-atom force field of van der Spoel et al. [74].

Simulations employed fully periodic boundary conditions in a cubic box of 17.63 nm per side (ca. 5929.7 nm³), containing 15C₆₀ molecules and the corresponding number of ethyl acetate molecules to achieve the target concentration. A 1.0 nm cutoff was used for both van der Waals and short-range Coulombic interactions; long-range electrostatics were treated with the Particle-Mesh Ewald (PME) method. All bonds involving hydrogen atoms were constrained with the LINCS algorithm.

Production runs were carried out in the canonical (NVT) ensemble for 50 ns at 295 K, maintained via the velocity-rescaling thermostat. Trajectory frames were saved every 1 ps during the interval from 10 to 40 ns for subsequent analysis. Prior to production, each system underwent a three-step equilibration protocol: 1 ns in NVT, 1 ns in the isothermal-isobaric (NPT) ensemble to adjust the box size, and a final 1 ns in NVT.

3. Results and discussion

3.1. The importance of sample concentration, preparation method and experimental conditions on the shape of the absorption spectra of C₆₀

The UV-vis absorption and fluorescence properties of C₆₀ have been studied in ethyl acetate (AcOEt), a solvent with low dielectric constant ($\epsilon = 6.053$) [75,76] where, in principle, C₆₀ should not present aggregation at concentrations of the order of 1–50 μM [33,34]. However, Fig. 1 shows the UV-vis absorption spectra of two samples of C₆₀ in AcOEt, at the same 20.7 μM concentration (a typical value used in photophysical studies) which display strikingly different shapes depending on the concentration and sonication time of the corresponding stock solutions (Sample 1 and Sample 2, in AcOEt saturated or supersaturated with C₆₀, respectively). The air-equilibrated stock samples in AcOEt were prepared by weighing the commercial solid to obtain either a 50.0 μM concentration (Sample 1, with 30 min sonication), resulting in a colorless solution to the naked eye, showing the typical UV-vis absorption spectrum of apparently dissolved C₆₀ (Fig. S1, Supporting Information) or, at a slightly higher 69.4 μM concentration (Sample 2) that, even after 1 h sonication, produced a supersaturated yellow dispersion peaking at 354 nm, with a prominent shoulder at 450 nm (Fig. S1, Supporting Information), attributed to C₆₀ aggregation

in a literature report where a [60]fullerene film on quartz and a solid sample on LiF were studied [77]. Detailed information regarding the experimental procedure for the preparation of samples, the spectral features of the stock samples and their corresponding dilutions, as well as a discussion about the Beer-Lambert linearity, correction of light-scattering and the role played by the molecular aggregates on the shape (bands/shoulders) and intensity of the UV-vis absorption spectra of C₆₀ in AcOEt has been included in the Supporting Information (Figs. S1, S2, S3, S4 and S5). Yet, the two spectra of Fig. 1 clearly suggest that the broader UV-vis and hyperchromic absorption bands observed in the sample prepared with the stock of higher concentration (Sample 2) are related to its poor solubility and the presence of intermolecular aggregates that, however, seem to disappear when diluted at 1.74 μM concentration (Fig. S1, Supporting Information).

Furthermore, since many photophysical studies require the use of samples prepared under inert atmosphere, the effect of sonication time, Ar-purge, and time elapsed between purge and acquisition of spectra of the purged sample was also tested with the yellowish sample 20.7 μM , where molecular aggregation is evident. Fig. 2A shows how 15 min sonication increases the typical absorption peak of C₆₀ at 328 nm at the expense of a decrease of the shoulders in the visible region and near 354 nm. Interestingly, Ar-purge has a similar effect to that of sonication, as shown in Fig. 2B by the higher hyperchromic effect at 328 nm along with the hypochromicity observed in the 340–520 nm interval. Fig. 2C shows that the gas purge effect is short-lived and reversible, as evidenced by the recovery of the spectral features associated with molecular aggregation if the spectrum under Ar is acquired again after a time lapse of 25 min. However, Fig. 2D shows hysteresis on this reversibility, probably due to the gas purge, since the UV absorption band and shoulder show a lower decrease compared to the increase of the visible band shoulder.

Fig. 3A and B displays, respectively, the UV-vis absorption spectra of C₆₀ either in AcOEt or in AcOEt-toluene mixture (12:1, v/v). The latter sample was obtained by addition of AcOEt to a stock sample prepared with commercial C₆₀ dissolved in toluene, $3.66 \cdot 10^{-4} \text{ M}$ (0.26 g L^{-1}), well below the solubility limit of C₆₀ in toluene (2.4 g L^{-1}) [30,31]. The spectra were recorded under air-equilibrated and Ar-purged conditions, with a sonication period of 15 min before the Ar-purge and spectra acquisition.

The air-equilibrated sample in AcOEt-toluene shows an absorption spectrum like that of C₆₀ in toluene (except for the lack of the absorption valley between 430 and 440 nm) [78,79], which is also similar to those spectra recorded with the dilutions of the 50.0 μM stock (see above and Fig. S1, Supporting Information). This sample also has the typical purple color of C₆₀ in toluene, with absorption coefficients ($\epsilon_{328 \text{ nm}} \approx 18900 \text{ M}^{-1} \text{ cm}^{-1}$, $\epsilon_{403 \text{ nm}} \approx 1800 \text{ M}^{-1} \text{ cm}^{-1}$ and $\epsilon_{532 \text{ nm}} \approx 700 \text{ M}^{-1} \text{ cm}^{-1}$) in good agreement with the literature values regarding their peak wavelength, though with slightly smaller ϵ values [78,79], still suggesting some influence of aggregation at the microscopic level even at a concentration as low as 27.4 μM . When comparing the UV-vis absorption spectra of the samples in AcOEt-toluene under Ar-purged or air-equilibrated conditions, similar spectra were obtained within experimental error in all cases, again suggesting the lesser influence of aggregation under these conditions.

Figs. 1–3, S1, S2, S3, S4 and S5, clearly show the irreproducibility risks concerning the acquisition of the UV-vis absorption spectra of C₆₀ in AcOEt, and, by extension, in any other organic solvent in which the solubility of C₆₀ is limited, since factors such as the sample concentration and its preparation procedure (i.e., sonication time or Ar-purge) can strongly affect the spectral shape.

As molecular aggregation at the nanoscopic level is the main cause of spectral irreproducibility in this type of samples, efforts to correct the absorption spectra for Rayleigh scattering influencing the relative intensity and position of absorption peaks and shoulders were carried out (Figs. S3, S4, S5, Supporting Information) [52,55,56]. However, our attempts failed due to overcorrection in the UV-blue side of the spectra,

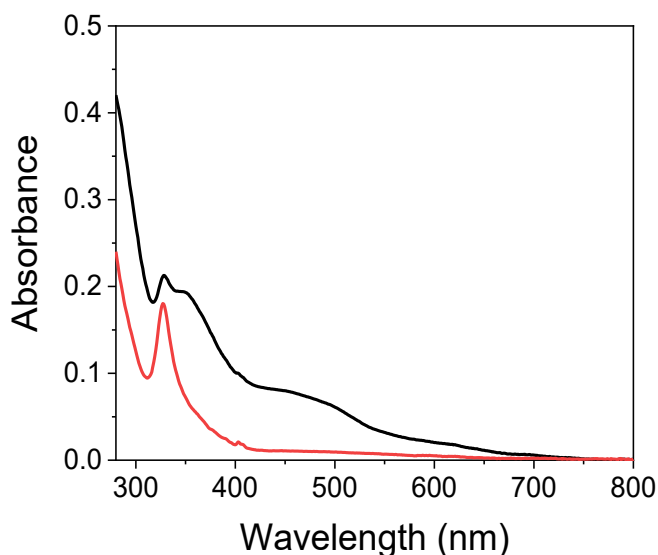


Fig. 1. UV-vis absorption spectrum of air-equilibrated 20.7 μM samples of C₆₀ in AcOEt prepared by dilution either of a 50.0 μM stock (30 min sonication, red) or a 69.4 μM stock (1 h sonication, black). Both samples were sonicated for 15 min prior to spectrum acquisition. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

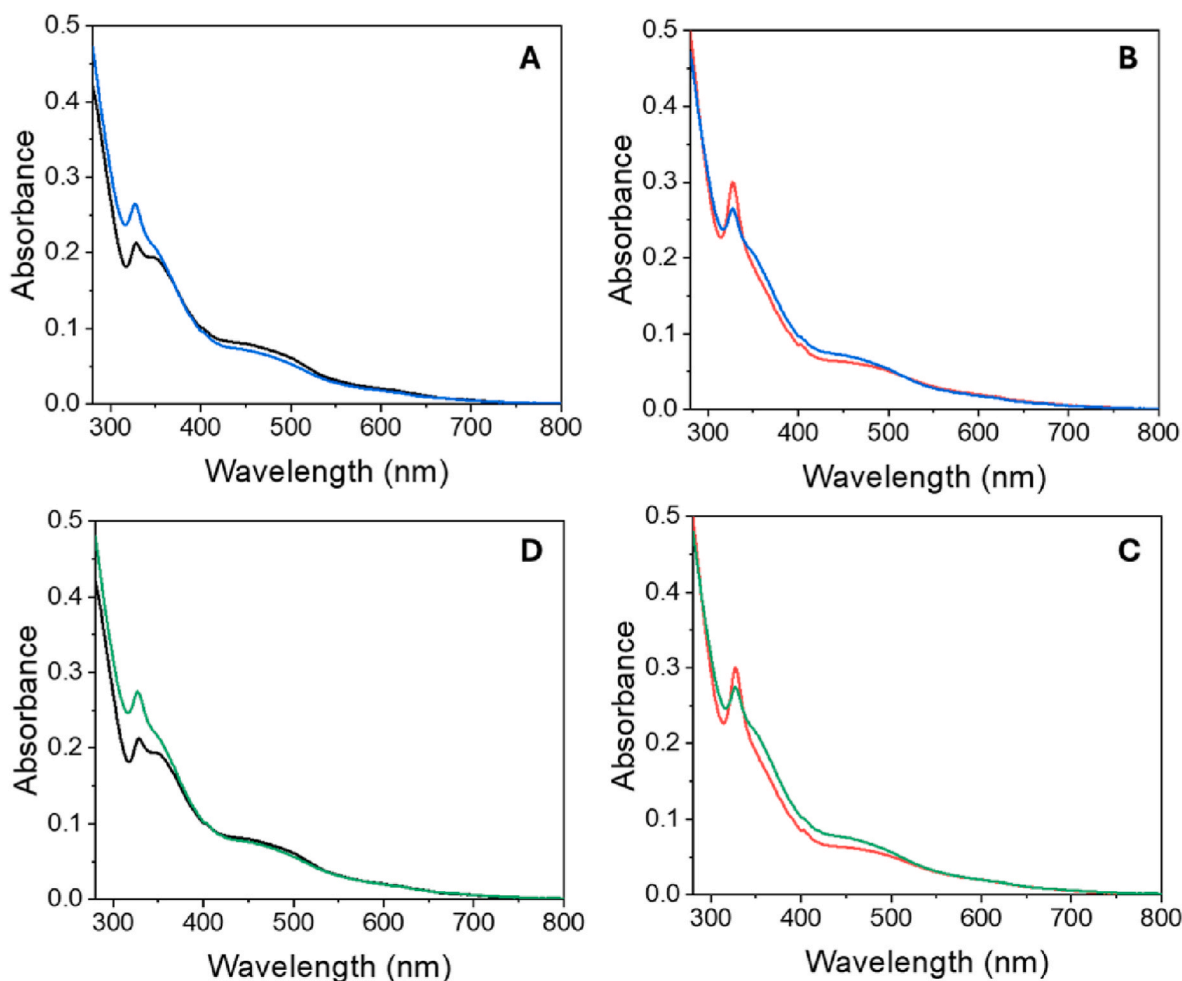


Fig. 2. Comparison among the UV-vis absorption spectra of C_{60} in AcOEt under different experimental conditions for the $20.7 \mu\text{M}$ sample prepared by dilution of a $69.4 \mu\text{M}$ stock (1 h sonication). The black spectrum (A, D) was obtained for the air-equilibrated sample without sonication prior to spectrum acquisition. The blue spectrum (A, B) was acquired for the air-equilibrated sample after sonication for 15 min prior to spectrum acquisition. The red spectrum (B, C) was obtained after sonication for 15 min prior to Ar-purge and spectrum acquisition. The green spectrum (C, D) was acquired 25 min after the acquisition of the red spectrum. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

which limited the possibility of reliably estimating the absorption coefficients of C_{60} in AcOEt with confidence. Therefore, for the determination of photophysical characterization data such as absorption coefficients or fluorescence quantum yields, detailed experimental procedures need to be provided.

3.2. Unconventional dual emission of C_{60} in ethyl acetate: the importance of sample concentration, experimental conditions and excitation wavelength, on the spectral shape and emission lifetimes of C_{60} fluorescence

Regarding the emission spectra (Fig. 3C and D), two bands with their corresponding shoulders were clearly observed in the 425–850 nm interval, both in AcOEt and AcOEt-toluene mixture. Similar spectral shapes but different intensity ratios were observed in Ar-purged or air-equilibrated suspensions, suggesting that the blue/red fluorescence bands were distinctly sensitive to the presence of molecular oxygen (i.e. O_2 -quenching of the blue emission but O_2 -insensitive red fluorescence). Therefore, at least two fluorescence emission bands can be detected in the UV-vis spectral range at ≈ 20 – $30 \mu\text{M}$ concentration. It should be noted that all fluorescence spectra were acquired by placing long-pass filters with cut-off wavelengths of 395 or 435 nm in the emission path, in order to completely eliminate Rayleigh scattered light from the excitation source. Considering that these 395 or 435 nm cut-off filters

eliminate not only scattered excitation light, but also part of the sample's fluorescence emission in the corresponding UV or blue regions, respectively, their use partially modifies the shape of the emission bands, reducing the fluorescence signal detected in the UV or blue region of the spectrum closest to the nominal cut-off wavelength of these filters. As a result, unconventional emission is not limited to the blue and green regions of the visible spectrum but also extends into the UV region, in excellent agreement with the literature reporting the fluorescence of solid samples of C_{60} [77]. No shift of $\lambda_{\text{em}}^{\text{max}}$ with λ_{exc} of the red band (typical of molecular C_{60}) was observed; however, the shape of the new fluorescence band showed an increasing habit from 650 nm to 400 nm and beyond in the UV region, in excellent agreement with previous literature on the photoluminescence of solid C_{60} excited with UV light [77]. Interestingly, when the effect of the UV excitation wavelength was explored in the 300–400 nm interval, using a long-pass filter with cut-on wavelength of 395 nm, a dependence of the red/blue-green bands ratio on λ_{exc} was observed, since $\lambda_{\text{exc}} = 300 \text{ nm}$ favors the blue-greenish emission, while $\lambda_{\text{exc}} = 373 \text{ nm}$ favors the red emission band (Fig. 4 and S6). On the other hand, the inner filter effects that can occur due to strong absorption at the excitation wavelength used, as well as the self-absorption of fluorescence in the visible interval, which are significant effects that cannot be ignored and are especially relevant when higher concentrations are used, explain why this secondary emission has not always been observed contingent on the sample concentration and

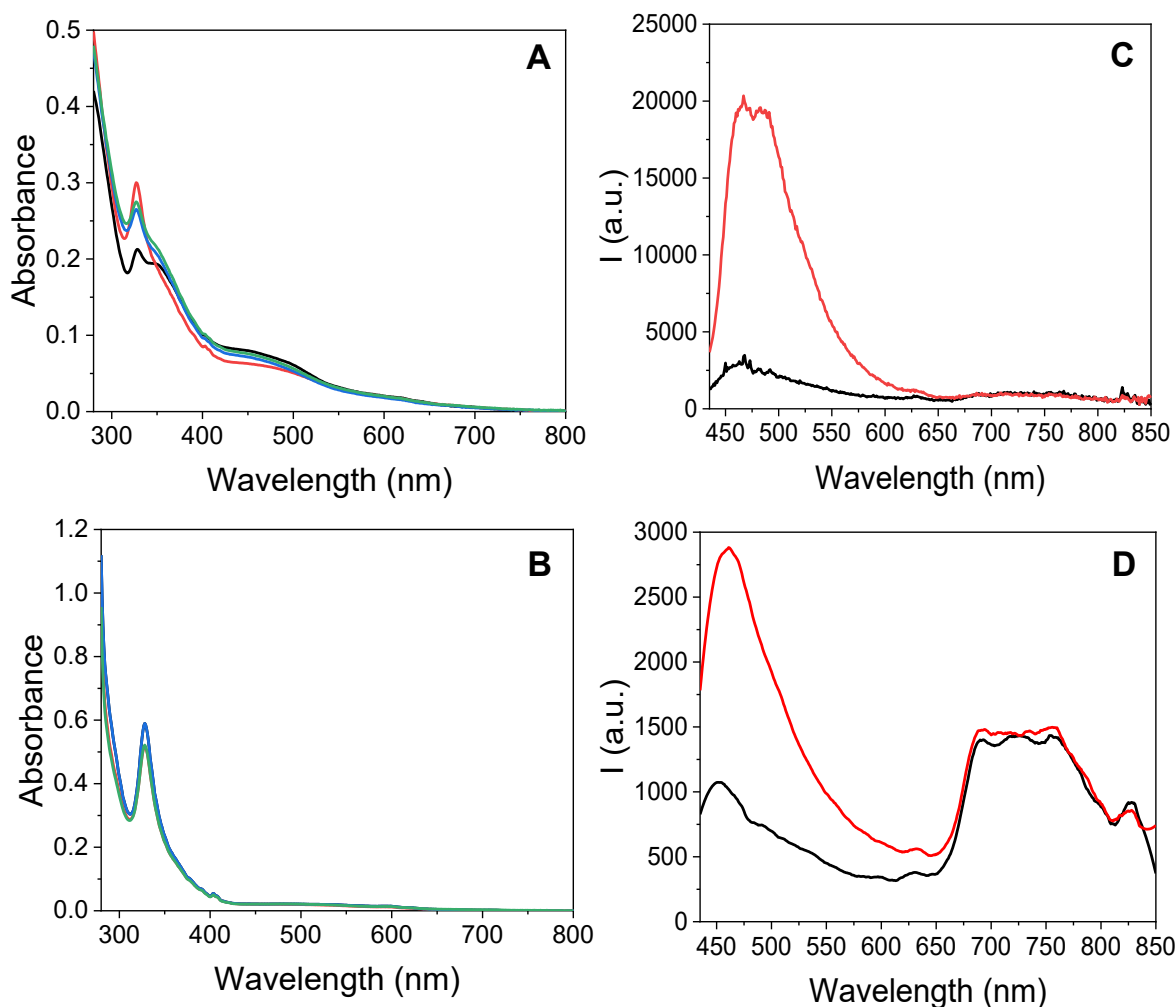


Fig. 3. UV-vis absorption and fluorescence spectra of C_{60} 20.7 μM (AcOEt, 69.4 μM stock; A, C, respectively) and 27.4 μM (AcOEt-toluene, 12:1, v/v; B, D, respectively). UV-vis absorption spectra A and B: Air-equilibrated suspension without sonication (black), Ar-purged suspension after sonication for 15 min prior to Ar-purge and spectrum acquisition (red), air-equilibrated suspension with 15 min sonication (blue), Ar-purged suspension as in the red spectrum but acquired with a time lapse of 25 min (green). Fluorescence spectra C and D: Air-equilibrated suspension (black), and Ar-purged suspension (red), after sonication for 15 min, recorded with the same acquisition parameters and corrections for solvent background and wavelength-dependent detector response (absorbance < 0.2 at $\lambda_{\text{exc}} = 373$ nm, long-pass filter with cut-on wavelength of 435 nm in the emission path). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

experimental setup, particularly with regard to the excitation wavelength used and the long-pass filters incorporated in the emission path of the fluorometer.

Remarkably, a concentration limit $\approx 2 \mu\text{M}$ has been observed for the detection of this new band with UV excitation (373 nm), suggesting that the absence or presence of the new UV/blue-greenish fluorescence band could be determined by an aggregation threshold (Fig. 5). This secondary emission could not be detected even with excitation of a 1.74 μM sample at 300 nm, where detection of the secondary unconventional emission should be optimal (see above and Fig. S7). Interestingly, this concentration threshold for observing C_{60} aggregation in ethyl acetate is very similar to the solubility value of C_{60} in acetone (1.4 μM) [31]. On the other hand, the analysis of the emission ratios, $I_{\text{em } 700 \text{ nm}}/I_{\text{em } 450 \text{ nm}}$ (Table S1), from the data of the fluorescence spectra in Fig. 5 at 700 nm (attributed to individual C_{60} units) and 450 nm (attributed to C_{60} aggregates), shows that this ratio increases with dilution, from 0.52 observed for the sample 10 μM to 4.82 determined for the sample 2 μM , suggesting a dynamic equilibrium between individual C_{60} units and their aggregates that depends on the concentration of C_{60} , and where dilution of the more concentrated C_{60} sample should reverse the equilibrium of association towards the formation of more individual C_{60}

units [$n C_{60} \rightleftharpoons (C_{60})_n$], in good agreement with the literature [40,80,81]. This reversible aggregation process where the C_{60} monomers exist in equilibrium with C_{60} aggregates also suggests that a critical (threshold) concentration of C_{60} is required for the formation of C_{60} aggregates, in excellent agreement with the literature as well [58,80,82,83]. Also interestingly, for a 6.94 μM C_{60} sample above the concentration threshold required for the observation of the secondary emission, a comparison between the UV-vis absorption and the fluorescence excitation spectra acquired at emission wavelengths of either 440 or 700 nm (Fig. S8), suggests that the contribution of the secondary unconventional emission to the excitation spectrum is dominant at wavelengths near 300 nm or below (308 nm and, mainly, 260 nm), in excellent agreement with results shown in Fig. 4 and with previous literature [77], while the contribution to the commonly observed red emission can be traced to excitation wavelengths above 300 nm, including the characteristic sharp peak of C_{60} at 328 nm that can be clearly seen in the excitation spectrum with detection at 700 nm, attributed to the emission from isolated C_{60} molecules (Fig. S8).

Time-resolved fluorescence measurements allowed the determination of the emission lifetimes (τ) of the main blue and red fluorescence bands for Ar-purged (τ_0) or air-equilibrated (τ_{air}) AcOEt and AcOEt-

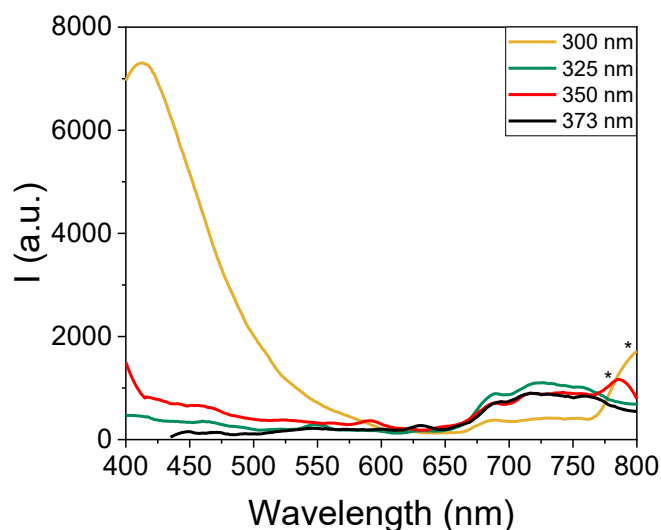


Fig. 4. Changes in the UV-vis fluorescence spectra of C_{60} 50 μM in air-equilibrated AcOEt with the excitation wavelength (300, 325, 350 or 373 nm, with absorbance <0.2 at the excitation wavelength and long-pass filter with cut-on wavelength of 395 nm in the emission path). The (*) denotes the harmonic of the emission band in the UV region (red and yellow spectra), which cannot be shown in the selected fluorescence wavelengths window (400–800 nm), due to the long-pass filter used. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

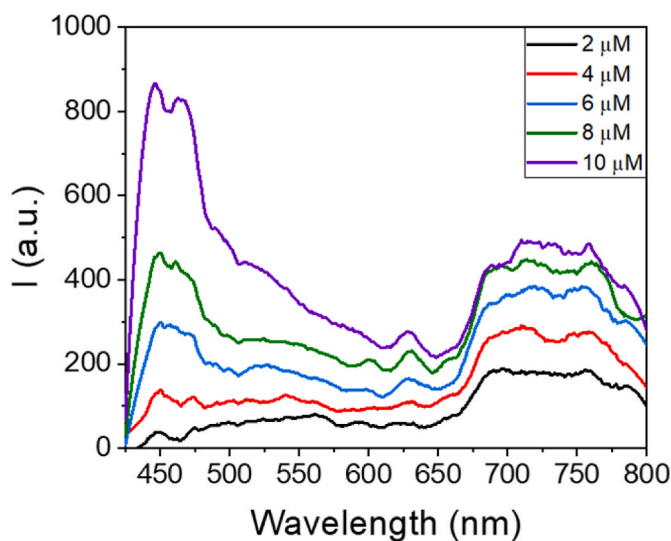


Fig. 5. Determination of the concentration threshold for the observation of the UV-vis fluorescence band of C_{60} in air-equilibrated AcOEt with an excitation wavelength of 373 nm (long-pass filter with cut-on wavelength of 435 nm in the emission path).

toluene solutions at $25 \pm 0.2^\circ\text{C}$. Results collected in Table 1 and S2 show that adequate fitting of the emission decay curves requires bi- or tri-exponential functions, and that the discrete lifetime components of the red band are more dependent on the sample concentration than on the excitation wavelength (373 or 478 nm), solvent polarity or the presence of molecular oxygen, in good agreement with the literature [13,45]; while the discrete lifetime components associated to the blue emission band show a larger dependence on the different experimental conditions tested, in good agreement with the limited reproducibility previously observed with the absorption and emission spectra, suggesting that the chemical entities responsible for this secondary emission

Table 1

Intensity-weighted average fluorescence lifetimes of C_{60} in AcOEt^a or AcOEt-toluene (12:1, v/v)^b for Ar-purged (τ_0) or air-equilibrated (τ_{air}) solutions at $25 \pm 0.2^\circ\text{C}$ (absorbance <0.2 at $\lambda_{\text{exc}} = 373\text{ nm}$).^c

Sample	τ_0 [ns]	τ_{air} [ns]	τ_0 [ns]	τ_{air} [ns]
λ_{em}	680	680	450	450
21 μM^a	1.6 ± 0.16	1.4 ± 0.14	11.5 ± 3.5	4.6 ± 1.38
12 μM^a	-	1.9 ± 0.57^d	-	2.4 ± 0.72^e
12 μM^a	-	2.1 ± 0.63^f	-	-
27 μM^b	1.7 ± 0.17	1.6 ± 0.16	8.2 ± 2.5	4.5 ± 1.35

^a Two concentrations, 21 μM and 12 μM , were tested in AcOEt.

^b 27 μM in AcOEt-toluene (12:1, v/v).

^c The discrete lifetime components and their % intensity or % amplitude contributions, average lifetimes and experimental uncertainties are reported in Table S1.

^d Detection wavelength, $\lambda_{\text{em}} = 670\text{ nm}$.

^e Detection wavelength, $\lambda_{\text{em}} = 440\text{ nm}$.

^f $\lambda_{\text{exc}} = 478\text{ nm}$, detection wavelength, $\lambda_{\text{em}} = 670\text{ nm}$.

are more sensitive to any experimental condition tested, including the polarity of the medium or the presence of additives such as molecular oxygen.

When the time-resolved fluorescence signal of C_{60} dispersions in AcOEt is detected in the red region (680 nm), the % I and % A of each discrete lifetime component are somewhat sensitive to fluorescence quenching by molecular oxygen (although this fact is slightly reflected in both average lifetimes, according to the short-lived nature of these emitting species, yielding a small singlet state quenching probability, P_{Q2}^S , below 12%). However, in the blue region (450 nm), where a very long-lived component (τ_1) is detected, not only the % I, % A and each discrete lifetime component (τ_1) but also the intensity-weighted ($\tau_{\text{AV INT}}$) or amplitude-weighted ($\tau_{\text{AV AMP}}$) average lifetimes are strongly affected by the presence of O_2 (P_{Q2}^S 60%). This result agrees well with the above-mentioned changes and wavelength dependence of the fluorescence spectrum in the presence of dioxygen (Fig. 3). Moreover, notice that no photophysical meaning can be attributed to each discrete decay factor since, otherwise, only the components with the longest lifetimes should be efficiently quenched by O_2 [54].

On the other hand, a 27 μM C_{60} dispersion in AcOEt-toluene, where C_{60} should solubilize better, was also investigated. The absorption spectra of this sample after sonication under Ar-purged or air-equilibrated conditions were identical within experimental error (Fig. 3B). However, the fluorescence spectra after sonication showed two main bands in the 425–850 nm interval, again evidencing the presence of at least two different emitting species that, once more, were differently quenched by O_2 in the region of blue fluorescence (Fig. 3D). In excellent agreement with these observations, the emission lifetimes reported in Table 1 and S2 in AcOEt-toluene show almost constant decay fitting parameters at 680 nm in Ar-purged or air-equilibrated conditions, with a negligible influence due to the presence of molecular oxygen (P_{Q2}^S 6%). In contrast, when measurements were performed at 450 nm, a strong impact is yet again observed due to the presence of O_2 (P_{Q2}^S 45%). Therefore, molecular oxygen quenches the fluorescence of C_{60} mainly in the UV/blue-greenish region, and this also justifies why this secondary emission has not always been observed depending on the experimental conditions tested. In summary, the unconventional emission from C_{60} aggregates shows longer emission lifetimes (τ_0 11.5 ns in AcOEt or τ_0 8.2 ns in AcOEt-toluene, in the 20–30 μM range) compared to the fluorescence lifetime of isolated C_{60} (ca. 1.7 ns in AcOEt or AcOEt-toluene) and, moreover, these longer lifetimes can be modulated by the dissimilar interactions experienced by the associated C_{60} molecules (among them, with solvent molecules or with excited state quenchers such as O_2), compared with the more homogeneous interactions occurring in the case of isolated C_{60} monomers. Similarly, several examples have been reported in the literature where longer emission lifetimes can be observed for distinct luminophores showing different types of intermolecular interactions, aggregation, or self-aggregation features

limiting the accessibility of solvent or quencher molecules towards them, and modulating their emission lifetimes and intensities depending on the degree of exposition of the luminophores to the solvent or to diffusing quencher molecules [52,84–87].

Time-resolved fluorescence anisotropy experiments were also performed to shed light on the size of the emitting fluorophores by measuring their corresponding rotational lifetimes [57]. [60]Fullerene has a van der Waals diameter of about 1.01 nm and a nucleus-to-nucleus diameter of about 0.71 nm [34,38,88–90], therefore, the size of the isolated C₆₀ fluorophore should indeed be below 1 nm, while other emitting species formed by aggregation of C₆₀ units should show fluorophore sizes above 1 nm. Interestingly, the fluorophore diameters estimated from our fluorescence anisotropy experiments differ when measurements were performed at emission wavelengths of 440 or 680 nm under the different conditions tested, suggesting emitting species with different nature (Table 2 and S3). When studying the red emission at 680 nm, the detected fluorophores show a size of about 0.5 nm, close to the upper limit of 0.70 nm for one C₆₀ unit (0.35 nm is the mean hydrodynamic radius of molecular C₆₀) [91], while in the case of the blue emission the estimated diameters are close to 2 nm, suggesting that several C₆₀ molecules could form the aggregates responsible for the blue fluorescence emission observed in AcOEt or AcOEt-toluene solvents, in excellent agreement with previous literature on C₆₀ aggregation where a size of 2.3 nm has been reported for C₆₀ aggregates in benzene [34,92], even reporting the expected strong absorbance increment around 2.8 eV (ca. 445 nm) as the cluster size increases, as we have also detected in AcOEt (see absorption spectra of Fig. 1 and S1, and computational section) [93].

These results suggest that in the case of [60]fullerene, where only a weak van der Waals interaction occurs between the C₆₀ units, the red fluorescence band can indeed be attributed to monomolecular emission, while the unconventional emission band can be attributed to nano-sized aggregates (≥ 2 nm) formed even in the low μ M concentration range. Furthermore, these intermolecular interactions cease to be effective in the 2–4 μ M interval, causing the disappearance of the unconventional emission (Fig. 5 and S7).

3.3. Computational analysis of C₆₀ in ethyl acetate solution

Driven by experimental evidence showing blue-light emission induced by the clustering of C₆₀ molecules, we have investigated fullerene aggregation through molecular dynamics (MD) simulations in AcOEt (Fig. 6A). Initially, a system comprising 15C₆₀ units was simulated at ca. 21 μ M to replicate experimental conditions. Consistent with observations, the C₆₀...C₆₀ radial distribution function (RDF) (Fig. 6B) exhibits a distinct sharp peak at 1 nm, signifying pronounced fullerene association, typically involving around four molecules. Additionally, smaller peaks at slightly greater distances (1.5 to 1.8 nm) suggest that these initial aggregates are not isolated but tend to associate, giving rise to larger, more loosely organized supramolecular assemblies containing up to nine C₆₀ molecules (Fig. 6C).

Notably, C₆₀...C₆₀ interactions occur directly, without intervening AcOEt molecules, and are mediated via π - π stacking between fullerene

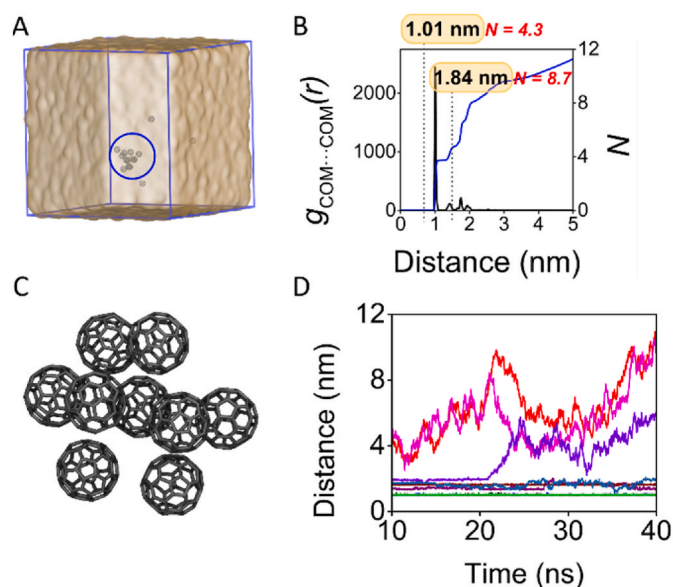


Fig. 6. Selected results taken from MD simulations. A) Representative snapshot of the 3D periodic simulation box used in the classical MD simulations (see Computational Details for further information). The yellow surface depicts the spatial distribution of solvent molecules, while the blue circle highlights the C₆₀ cluster (as shown in Fig. 6C). B) Radial distribution function (RDF) (black line) and its integration (blue line) between the centers of mass (COMs) of all fullerene pairs. The grey dashed line indicates the integration cut off distance, printed on the plot, with the integrated value shown in red. C) Representative snapshot of a nine-fullerene cluster. D) Time evolution of the intermolecular distance for a selected fullerene. Most C₆₀ molecules remain within 2 nm of each other throughout the simulation, although a few show minimal aggregation. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

surfaces. As shown in Fig. 6D, this multimeric assembly remains stable throughout the entire simulation trajectory.

One of the key insights derived from experimental observations concerns the estimated size of the fluorophore. Although our simulations do not explicitly account for excited states or their relaxation dynamics, they do allow for the estimation of the hydrodynamic volume of the clusters, which correlates with the data from experimentally measured rotational lifetimes. Based on this, we determined the hydrodynamic diameters of different assemblies as a function of their aggregation number (Table S4), leading us to conclude that the active (C₆₀)_n fluorophore likely comprises between 3 and 5 units.

With this in mind, we selected representative structures of a monomer, a tetramer, and a nonamer to perform ZINDO and DFT calculations. These were aimed at probing the electronic and photophysical properties of the system under study, and at understanding how molecular clustering influences them. The absorption spectra of the oligomers are presented in Fig. 7A. As the aggregate grows in size, the emergence of an increasing number of accessible excitonic states, which enable transitions to progressively lower-energy electronic levels, is observed. These theoretical findings align with experimental trends observed in AcOEt, where UV absorption diminishes (hypochromism) while a new, more intense shoulder emerges around 450 nm. This spectral evolution suggests the activation of additional absorption modes triggered by molecular aggregation.

Building on these results, we performed single-point DFT calculations on both the monomer and the tetramer to explore, in a qualitative sense, how aggregation affects the electronic structure. Fig. 7B displays the frontier orbital diagrams for each system. Within a ± 1 eV window around the HOMO and LUMO levels, the tetramer reveals a denser array of nearly degenerate orbitals. This broadened landscape of orbitals increases the number of plausible HOMO-X to LUMO + Y transitions,

Table 2

Estimated fluorophore diameter from rotational lifetimes of C₆₀.^a

Solvent	Size of the fluorophore [nm] ^d	
	Red fluorescence band	Blue fluorescence band
AcOEt ^b	0.47 $\pm$ 0.04	2.2 $\pm$ 0.4
AcOEt-toluene ^c	0.65 $\pm$ 0.10	2.0 $\pm$ 0.1

^a 25 $\pm$ 0.2 °C, absorbance <0.2 at λ_{exc} = 373 nm.

^b 21 μ M in AcOEt.

^c 27 μ M in AcOEt-toluene (12:1, v/v).

^d Rotational lifetimes and estimated hydrodynamic volumes and radii of the fluorophores are collected in Table S3.

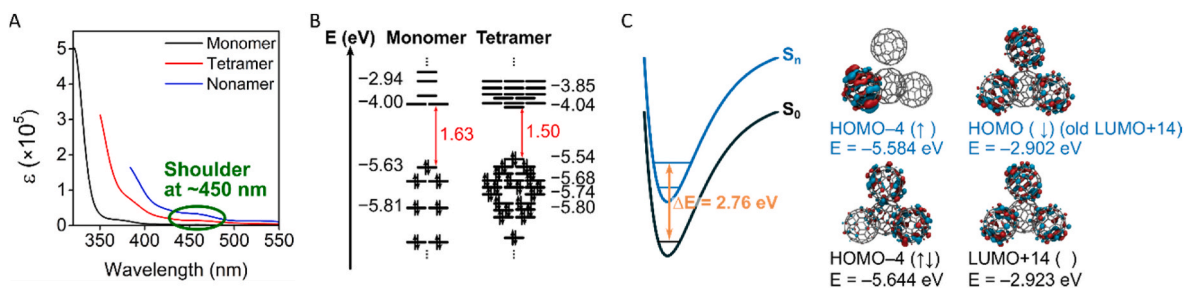


Fig. 7. Selected results from QM calculations. A) Absorption spectra of the monomer, tetramer, and nonamer, obtained from ZINDO calculations on representative MD snapshots. B) Frontier molecular orbital diagrams comparing the monomer and tetramer, calculated at the DFT level (PBE/def2SVP). C) Representation of the molecular orbitals involved in blue emission for both the ground state (S_0) and the excited state (S_n). The excited state was constructed by applying the electronic transition corresponding to the absorption wavelength of a blue-emitting photon (see the Computational Details section for more information). The spin density associated with the S_n state is shown in the Supporting Information (Fig. S9). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

reinforcing the hypothesis of larger number of accessible excitonic states and pointing toward mechanisms that could promote blue-region emission.

To probe this idea further, we estimated the energy and the nature of a possible excited S_n state responsible for a blue emission. Specifically, we selected the HOMO-4 to LUMO+14 excitation in the $(C_{60})_4$ tetramer, as it corresponds to one of the transitions with the largest oscillator strength within the blue region of the absorption spectrum, and compared it to the ground state. The excited-state geometry was not optimized. A visual representation of this process is provided in Fig. 7C, which suggests the generation of a charge-separated state. In fact, we have analyzed the variation of charge densities between the excited and the ground state using Mulliken charges and found changes up to 0.21e for some of the C_{60} units within the tetramer (Table S5). Besides, the root-mean-square of the charge variation for each of the four C_{60} units show values in the range 0.014–0.032. Therefore, we could describe such a state as a Wannier-like delocalized exciton [93]. If emission were to occur from a S_n state like this one, with an energy difference from S_0 of $\Delta E = 2.76$ eV, a band centered in the blue portion of the spectrum would be observed.

In summary, this exploratory approach illustrates how C_{60} aggregation in AcOEt may give rise to new electronic transitions and stabilize excited states conducive to blue emission.

4. Conclusion

[60]Fullerene shows a characteristic faint red fluorescence in benzene-like solvents. In this report we have studied, in the micromolar concentration range typically used in photophysical characterization measurements, the rarely reported UV/blue-greenish emission of C_{60} . This unconventional fluorescence can be associated with C_{60} aggregates (≥ 2 nm in size) formed by weak van der Waals (π - π) intermolecular interactions occurring even at concentrations well below the solubility limit of C_{60} in a given solvent, as suggested by the results of steady-state and time-resolved fluorescence anisotropy measurements and by theoretical calculations.

The unconventional emission has been detected in ethyl acetate and in its mixture with toluene, and depends on several factors that cannot be neglected, such as sample concentration and sonication, solvent polarity, and the presence of additives such as Ar inert gas or O_2 , as well as on the experimental setup of the fluorometer (excitation wavelength and selected emission filters). Since the fluorescence intensity ratios and emission lifetimes of the unconventional emission band depend on the aforementioned factors, accurate and reproducible detection of this secondary fluorescence can be a serious challenge unless the experimental conditions used are described in detail.

The unconventional fluorescence of C_{60} always shows longer emission lifetimes compared to the common red fluorescence generally

described for C_{60} . Protection of the aggregated fluorophore from deactivation by solvent molecules or quenching by dioxygen justifies the differential modulation of the potentially strong fluorescence band detected in the UV/blue-greenish spectral range, which is detected only over 2 μ M concentration in ethyl acetate.

In summary, the intriguing and long-standing open question regarding the additional emission of C_{60} has been clarified in terms of the potentially dominant π - π van der Waals interactions, which are responsible for the specific intermolecular association of [60]fullerene, resulting in the formation of emerging, unconventional, nanometer-sized fluorophores. Theoretical analysis confirms the stability of such small aggregates and shows that clustering increases the density of electronic states, enabling blue-region emission through charge-separated excited states within fullerene multimers.

This unconventional fluorescence, which occurs due to the aggregation of C_{60} molecules and may depend on various factors, could be exploited for developing new applications such as information encoding systems, anticounterfeiting, fluorescent probing or photosensitization based on the singlet exciton of $(C_{60})_n$.

Data availability statement

The data that support the findings of this study are available in the supplementary material of this article.

CRediT authorship contribution statement

Antonio Ribeiro-González: Investigation, Methodology, Writing – original draft. **Albert Masip-Sánchez:** Investigation, Methodology, Writing – original draft. **Josep M. Poblet:** Funding acquisition, Resources, Software, Supervision, Validation, Visualization, Writing – review & editing. **Antonio Rodríguez-Fortea:** Data curation, Formal analysis, Funding acquisition, Resources, Software, Supervision, Validation, Visualization, Writing – review & editing. **Santi Nonell:** Conceptualization, Funding acquisition, Writing – review & editing. **Beatriz María Illescas:** Conceptualization, Funding acquisition. **Nazario Martín:** Conceptualization, Funding acquisition, Project administration, Writing – review & editing. **David García-Fresnadillo:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.carbon.2026.121649>.

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