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► **To cite this version:**

Xavier Mercier, Olivier Carrivain, Cornélia Irimiea, Alessandro Faccinnetto, Eric Therssen. Dimers of polycyclic aromatic hydrocarbons: the missing pieces in the soot formation process. *Physical Chemistry Chemical Physics*, 2019, 21 (16), pp.8282-8294. 10.1039/c9cp00394k . hal-02299005

HAL Id: hal-02299005

<https://hal.science/hal-02299005>

Submitted on 27 Sep 2019

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1 **Title: Dimers of Polycyclic Aromatic Hydrocarbons: the Missing**

2 **Pieces in the Soot Formation Process**

3
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17
18 **Abstract:**

19 The soot nucleation process, defined as the transition from molecular precursors to condensed
20 matter, is the less understood step in the whole soot formation process. The possibility that
21 polycyclic aromatic hydrocarbon (PAH) dimers, especially those involving moderate-sized
22 PAHs, can play a major role in soot nucleation is a very controversial issue. Although PAH
23 dimers have often been considered as potential soot precursors, their formation is not
24 thermodynamically favored at typical flame temperature, their binding energies being
25 considered too weak to allow them to survive in this environment. Hereby, we report
26 experimental evidence highlighting the existence of PAH dimers in the proximity of the soot

27 nucleation region of a methane laminar diffusion flame that give strong evidence for the
28 nucleation process to be kinetically rather than thermodynamically controlled.

29

30 **Keywords:** soot nucleation, polycyclic aromatic hydrocarbons (PAHs), dimers of PAHs, laser
31 induced fluorescence (LIF)

32

33

34

35 **1. Introduction:**

36 Soot emissions are a major source of natural and anthropogenic atmospheric pollution
37 well known for having a measurable impact on human health and environment ¹. It is
38 common knowledge that soot is formed during the incomplete combustion of hydrocarbons.
39 However, a detailed and comprehensive understanding of the fundamental mechanisms of
40 soot formation has not been reached yet. Over the last decades, numerous works focused on
41 the determination of the chemical mechanisms governing soot formation through the
42 identification of the involved species ^{2,3}. Some key steps of these mechanisms have been
43 established that highlighted the central role of polycyclic aromatic hydrocarbons (PAHs).
44 PAHs formed during the combustion process are mainly issued from reaction pathways
45 involving benzene according to a major chemical growth process known as HACA
46 mechanism ⁴, and are well known to contribute to the inception of soot particles. However,
47 the soot nucleation process, corresponding to the transition from gaseous molecular
48 precursors to condensed matter, is still mostly unknown ⁵. Many kinetic models that simulate
49 soot formation invoke the dimerization of small PAHs up to 4-5 aromatic rings as the
50 elementary building block of soot particles. Nevertheless, this hypothesis is generally
51 considered as a mere numerical tool rather than realistically mirroring a physical
52 phenomenon. The physical reality of dimerization is usually ruled out because of the
53 weakness of PAH-PAH interactions, along with detailed calculations showing dimers of
54 moderate-sized PAHs to be thermodynamically instable at flame temperature ⁵. From
55 theoretical calculations based on thermodynamic considerations, only PAHs as large as
56 ovalene (C₃₂H₁₄) or circumcoronene (C₅₄H₁₈) may lead to the formation of dimers capable to
57 survive at flame temperature ^{5,6}. However, the amount of soot particles measured in sooting
58 flames is several orders of magnitude higher than typical concentrations of such large PAHs ⁷.
59 The implication of dimers of PAHs of this size in the soot nucleation process appears

60 therefore highly unlikely^{5,7}. Other hypotheses relying on the chemical coalescence of PAHs
61 into cross-linked three-dimensional structures has also been proposed⁸. This pathway requires
62 numerous H atoms to generate aryl radicals by hydrogen abstraction, capable to react with
63 aromatic molecules to form such three-dimensional structures. However, this mechanism has
64 also been proven inadequate to explain the nucleation at low temperature where H abstraction
65 is limited as well as the persistent nucleation observed into the burnt gases of premixed
66 flames^{9,10}.

67 Primary soot particles are organized in a quasi-amorphous central core surrounded by
68 concentric graphene-like layers^{11,12}. Nascent soot particles (NSPs) are less carbonized than
69 mature soot and show a significantly different structure characterized by clusters with
70 randomly distributed orientation inside the core, and can be as small as 1-3 nm¹³. This size
71 has been shown to be consistent with clusters of PAHs containing up to 5 aromatic rings and
72 20 carbon atoms^{14,15}. Finally, NSPs are characterized by lower density, closer to the density
73 of moderate-sized PAHs as pyrene (1.27 g/cm³) rather than mature soot (1.80 g/cm³)¹⁶,
74 indicating that a graphitization/dehydrogenation process takes place during the soot growth
75 process.

76 These data strengthen the idea that clusters of moderate-sized PAHs may be involved
77 in the nucleation process, despite the unfavorable thermodynamic conditions for their
78 formation at flame temperature. Herdman and Miller¹⁷ used density functional theory (DFT)
79 calculations to estimate the intermolecular potentials of PAH clusters to define the size
80 threshold beyond which PAH dimers can be formed in flames. Calculated data¹⁷ suggest that
81 the binding energy of many pericondensed PAHs, including moderate-sized PAHs, may be
82 large enough to form dimers at flame temperature. However, Wang⁵ revisited these
83 conclusions by considering the entropy resistance to the binding that can prevent dimerization
84 even if the binding energies are large enough. Wang⁵ thus defined an equilibrium constant for

85 the dimerization and concluded that only PAHs as large as circumcoronene ($C_{54}H_{18}$) can
86 survive in a flame environment. Nevertheless, in this approach, dimerization was always
87 considered to be thermodynamically controlled.

88 To allow the formation of dimers of moderate-sized PAHs in flames, an emerging
89 theory suggests that nucleation might be governed by kinetics rather than thermodynamics.
90 Schuetz and Frenklach¹⁸ first considered this hypothesis. Notably, they showed by non-
91 equilibrium molecular dynamics simulations that the lifetime of pyrene dimers might be
92 greatly enhanced by the deposition of energy into internal rotations in the colliding pair of
93 pyrene under flame conditions. In this framework, dimers may survive long enough to evolve
94 into NSPs. This idea was elaborated in kinetic models of soot formation in recent papers.
95 Notably, Eaves et al.^{15,19} introduced the reversibility of the nucleation based on the
96 dimerization of PAHs sizing from naphthalene up to benzo(a)pyrene. Aubagnac-Karkar et al.
97²⁰ used the hypotheses of the reversibility of the nucleation and pyrene dimerization to
98 successfully reproduce soot volume fraction profiles experimentally measured in five
99 premixed flames characterized by different equivalence ratio, fuels and pressure conditions
100 leading to a variation of seven orders of magnitude between the numerical results and the
101 experimentally obtained soot volume fractions. More recently, Kholghy et al.²¹ used the
102 dimerization of small to moderate-sized PAHs in their kinetic model, that also considers the
103 reversible formation of PAH clusters by van der Waals forces. In particular, they advocate
104 dimer stabilization through the formation of covalent carbon-carbon bonds following two
105 hydrogen abstractions from the monomers in a dimer. Both approaches show very good
106 agreement of the calculated and experimental soot volume fraction profiles for different
107 flames. They also show that only small to moderate-sized PAHs are sufficient to model soot
108 volume fraction profiles in agreement with the experimental data. Finally, in a very recent
109 paper, Johansson et al.²² highlighted that dimers of PAHs may be stabilized into covalently

110 bound cluster at high temperature according to a rapid radical-driven hydrocarbon clustering
111 mechanism and lead to the formation of soot particles. This work provides another consistent
112 explanation for the existence and the potential role of dimers of PAHs in the soot nucleation
113 process.

114 However, so far no clear experimental evidence on the formation of dimers of
115 moderate-sized PAHs has ever been given in the literature. Such evidence is therefore highly
116 needed, given their potential role as cornerstones of the soot nucleation processes. The
117 absence of experimental evidences most likely comes from the practical difficulty of
118 preserving the dimers during the preparation of samples for online or ex-situ measurements,
119 thus probably precluding the use of techniques as gas chromatography (GC) or mass
120 spectrometry (MS) that are otherwise widely used for the detection of PAHs in flames.
121 Because of their short lifetime in flames, dimers of PAHs likely require in-situ techniques as
122 laser diagnostics to be detected.

123 The spectroscopy of dimers of PAHs has been extensively studied in condensed phase
124 ²³ and supersonic expansions ²⁴. The UV excitation of these species leads to the formation of
125 excimers (dimers in an excited state) characterized by intense, broad and featureless
126 fluorescence emission in the visible spectral range. Dimers of PAHs share electronic
127 excitation transitions with the corresponding monomers, but their emission spectra are
128 systematically shifted toward higher wavelengths ²⁵.

129 The observation of broadband and unstructured visible emission spectra under UV and
130 visible excitation in sooting flames is not new. Early mentions date back to the 1980s ^{26,27} and
131 were first attributed to PAHs like acenaphthylene and fluoranthene. In a previous work, we
132 explored the possibility of excitation of such moderate-sized PAHs to explain the origin of
133 this visible fluorescence emission ²⁸. However, acenaphthylene is characterized by a very
134 weak fluorescence quantum yield ²⁹ while fluoranthene does not fluoresce far in the visible as

135 we show below in this paper. At present, the most commonly accepted explanation for these
136 experimental emission spectra measured in the visible range relies on the idea that larger
137 PAHs are characterized by fluorescence emission progressively extended toward higher
138 wavelengths³⁰. Hence, fluorescence above 450 nm is generally attributed to PAHs constituted
139 of more than 4 aromatic rings. In this paper, we demonstrate that this hypothesis is also very
140 unlikely. Finally, a few papers in the literature exist supporting the idea that these signals
141 could be issued from the fluorescence of dimers of PAHs^{31,32}. Miller et al. provided
142 convincing insights by DFT calculation that the broadband visible emission can be attributed
143 to aromatic excimers^{17,31}. More recently, Sirignano et al. carried out a series of experiments
144 in a sooting flame also suggesting the possibility that the visible emission fluorescence might
145 be characteristic of large PAHs and small clusters (dimers or trimers) of PAHs³².

146 Our present work aims to clarify the origin of the intense visible emission spectra
147 observed in sooting flames under laser excitation and consequently prove the existence and
148 the critical implication of dimers of moderate sized PAHs in the nucleation of NSPs. This
149 demonstration is based on the analysis of laser induced fluorescence (LIF) experiments
150 performed in a co-flow laminar diffusion methane-air flame. The analysis of the emission
151 fluorescence has been provided thanks to a simple spectroscopic model capable to simulate
152 these spectra. This model relies on the use of a spectral database, described below, enabling
153 the simulation of the measured fluorescence spectra measured from the flame. This analysis
154 clearly reveals two kinds of fluorescent species that are attributed to PAH monomers and
155 dimers, and discriminated by their different spectroscopic signatures.

156

157 **2. Experimental Setup**

158 LIF measurements have been carried out in the centerline of a methane/air co-flow
159 diffusion flame at atmospheric pressure. The soot inception region has been identified by laser

160 induced incandescence (LII) to begin around 60 mm height above the burner (HAB)³³. The
161 experimental configuration of the LIF measurements is shown in **fig. 1**. The flame was setup
162 on a modified McKenna burner, where the porous plug has been replaced with a central tube
163 (d=10.25 mm) which allows the injection of methane. The outer air flow tube (d=88 mm)
164 produces a homogenous air shield on account of a layer of glass beads placed between the
165 central injector and the burner edges. A 120 mm height non-smoking laminar diffusion flame
166 is stabilized using 0.52 L min⁻¹ of CH₄ and 87 L min⁻¹ of air. The burner and flame
167 configuration are described in detail in Irimiea et al.³⁴.

168 The excitation source consisted of a Nd:YAG laser (Quanta-ray, Spectra Physics),
169 generating laser pulses at 1064, 532 and 355 nm (pulse length 6 ns) which are mixed and used
170 to pump an OPO (premiScan-ULD/240, GWU-Lasertechnik) and provide wavelengths tunable
171 from 213 to 532 nm. LIF measurements have been performed at 213.5, 282, 405, 488 and 532
172 nm excitation wavelengths. After the laser output, the laser beam was slightly focused at the
173 center of the diffusion methane/air flame using a spherical UV lens (f=1000 mm). The laser
174 beam diameter at the probed volume has been estimated to be 500 μm. The output laser fluence
175 was adjusted with an attenuator for each excitation wavelength, in order to maintain its value
176 below the saturation threshold and to avoid interference with the LII signal. Typically, the
177 measurements have been performed for fluence below 20 mJ cm⁻². The absence of LII signal
178 has been systematically checked for each wavelength in the sooting region of the flame around
179 80 mm above the burner.

180 The emitted fluorescence was collected at a right angle with two spherical lenses
181 (diameter= 50 mm, and focal length = 100 and 75 mm, respectively) and imaged into a bundle
182 of optical fibers (diameter = 1.25 mm) connected to a spectrometer (IHR320, Jobin Yvon). The
183 spectrometer was equipped with a 100 grooves/mm grating blazed at 450 nm. The fluorescence
184 spectra have been recorded using a 16 bit ICCD camera (PI-MAX 2, Roper Scientific) coupled

185 to the spectrometer. The gatewidth (GW) of the intensifier was fixed at 40 ns. Prompt and
186 delayed fluorescence measurements after the laser pulse have been performed as discussed
187 below to discriminate the fluorescence signals issued from the PAHs and dimers of PAHs. The
188 spectral resolution of our detection system was 0.7 nm/pixel. The LIF decay signal at specific
189 wavelengths was also recorded with a photomultiplier tube (XP2020Q, Photonics). The
190 scattered laser light was removed by a WG 295 filter for laser wavelengths lower than 300 nm
191 or by notch filters for laser wavelengths higher than 400 nm (405, 488 and 532 nm). The
192 spectrometer has been wavelength-calibrated using the spectral lines from a mercury pen lamp.
193 The fluorescence spectra were corrected for the spectral intensity response of the detection
194 system (lenses, fiber, grating and camera) by the means of a uniform light source (CSTM-LR-
195 6-M, SphereOptics).

196 Laser induced incandescence (LII) experiments were performed at 1064 nm using the
197 fundamental of a pulsed Nd:YAG laser (Quantel Brilliant B, 6 ns pulse width, 10 Hz), already
198 reported in a previous paper³³. Soot particles were heated below the sublimation threshold
199 with a top hat profile at a fluence of 130 mJ cm⁻² and a square shape of the laser beam profile
200 (1x1,1 mm). The LII emission was recorded at 90° incidence with respect to the laser beam
201 propagation, using a system of two achromatic lenses for the imaging of the selected volume
202 at the entrance of a spectrometer equipped with a 150 grooves mm⁻¹ grating blazed at 300 nm.
203 A fast ICCD camera (Princeton Instruments PIMAX) placed at the exit of the spectrometer
204 recorded an image corresponding to 500 laser shots. The LII detection was performed during
205 50 ns GW after the peak of the laser pulse. In this case, the LII emission spectra were
206 recorded in the 580-800 nm wavelength range, with a filter that cut all the emission below
207 500 nm. This way the contribution of the second emission order of the grating in the visible
208 recorded domain was minimized. The spectral response of the detection system was calibrated

209 in intensity and wavelength using a similar procedure to the LIF measurements. The LII
210 signal was integrated over 5 nm wavelength range centered at 750 nm.

211

212 **3. Results and discussion**

213

214 **3.1 Experimental spectra**

215 Experimental fluorescence spectra measured with UV and visible excitation at different
216 HAB are shown in **fig. 2** and **fig. 3**, respectively. Spectra in **fig. 2a** show the raw intensity to
217 highlight the predominance of the visible emission between 400 and 600 nm above 40 mm
218 HAB. The contribution of UV emission between 300 and 400 nm below 40 mm HAB is better
219 highlighted in **fig. 2b**, in which all the spectra have been normalized to unit maximum. Hence,
220 in **fig 2b**, below 20 mm HAB only UV emission signals appear. This UV emission becomes
221 progressively less dominant as the visible emission rises at higher HAB, leading to a global
222 broadening and shift of the fluorescence to higher wavelengths. The fluorescence spectra
223 obtained at the excitation wavelength 405 nm, 488 nm and 532 nm are reported in **fig. 3**. The
224 fluorescence spectra recorded at 405 nm excitation wavelength correspond to a particular
225 case, characterized by a first emission band centered around 450 nm and slightly shifting
226 toward higher visible wavelengths at higher HAB. This specific case is discussed in detail in
227 the next section. The two other sets of spectra recorded at 488 nm and 532 nm excitation
228 wavelength do not show any spectral evolution against HAB in strong contrast with the
229 spectra recorded with UV excitation (**fig. 2**). The spectral structure measured at 488 nm
230 excitation wavelength shows a maximum intensity centered around 510 nm, while the
231 maximum intensity of the spectra obtained at 532 nm excitation is slightly red-shifted at 560
232 nm.

233

234 **3.2 Basics of the method for the analysis of the fluorescence emission spectra**

235 In the literature, the analysis of fluorescence spectra obtained with UV excitation in
236 sooting flames is generally carried out by attributing different spectral ranges of the measured
237 spectra to the emission of different classes of PAHs^{30,35}. The following classification is
238 commonly adopted: 2-3 rings PAHs are considered to fluoresce at 320-380 nm, while PAHs
239 with 4 and more rings are expected to fluoresce above 400 nm. Although this approach
240 provides an approximated discrimination of different classes of PAHs according to the size of
241 their aromatic system, it only enables a partial interpretation of the fluorescence spectra,
242 which is essentially limited by the possibility of overlap of different PAHs spectral
243 contributions. To address this issue and get a more accurate interpretation of the fluorescence
244 spectra, an original approach is hereby proposed that relies on the simulation of the
245 fluorescence spectra with a database containing fluorescence spectra of PAHs and dimers of
246 PAHs issued from the literature

247

248 ***3.2.1 Spectroscopy-based arguments supporting PAH dimerization in flames***

249 The spectroscopy of PAH monomers is dominated by π^* - π transitions, characterized by
250 intense absorption bands in the UV region (200-300 nm), which shift and broadens toward
251 longer wavelengths as the size of aromatic system increases. The corresponding fluorescence
252 emission spectra of these species are characterized by emission bands in the spectral range
253 300-450 nm. Shifting the excitation wavelength to the visible region therefore provides an
254 efficient way to selectively excite the largest PAHs. However, only a very limited number of
255 PAHs expected to be formed in flames are able to absorb above 400 nm^{29,36,37}. According to
256 these last references, no PAH up to coronene possess strong enough absorption bands above
257 450 nm, which could explain the intense fluorescence emission in the visible region measured
258 in sooting flames at visible wavelength excitation. Hence, PAH monomers cannot be
259 responsible of the strong fluorescence emission in the visible region recorded for instance at

260 488 or 532 nm excitation wavelength. Moreover, usual PAHs spectral properties are not
261 consistent with the wavelength range (450-700 nm) of the fluorescence emission signal
262 measured for high HAB in the flame. By contrast, dimers of moderate-sized PAHs, studied in
263 liquid phase have been shown to possess strong absorption features in this visible region ³⁸.
264 Although the spectroscopic schemes for such excitation wavelengths are not yet fully
265 understood, clear experimental evidences have been reported ³⁸, notably for the dimers of
266 pyrene and perylene, that highlight intense fluorescence emission following excitation at 488
267 nm and 532 nm. The corresponding fluorescence emission spectra are characterized by Stokes
268 and anti-Stokes spectral features around the excitation wavelength, very similar to the spectra
269 measured in sooting flames.

270

271 ***3.2.2 LIF spectral modeling***

272 In order to interpret the experimental emission fluorescence spectra measured in the
273 flame, we have developed a spectroscopic model capable to simulate these spectra. This
274 simulation code relies on a database containing the excitation and emission fluorescence
275 spectra of twenty pericondensed PAHs, from naphthalene (C₁₀H₈) to coronene (C₂₄H₁₂), listed
276 in **table 1**. We chose these PAHs as they represent the most stable and preferentially formed
277 PAHs in sooting flames according to the HACA mechanism that is the preferential chemical
278 route for the PAHs growth in sooting flames ³⁹. In the database, we did not include spectra of
279 PAHs larger than coronene, as such large PAHs are expected to form in very small quantities,
280 not consistent with the intense LIF signals observed in sooting flames.

281 We also considered the contribution of dimers of PAHs expected to form in flames in
282 sufficient concentration, i.e, dimers of moderate-sized PAHs also listed in **table 1**. Hence, five
283 homodimers of PAHs, from anthracene to benzo(ghi)perylene, have been taken into account.
284 It is noteworthy that, although heterodimers may also form in flames ⁴⁰, the lack of

285 spectroscopic data effectively prevents their use in this work. LIF spectra are modeled
286 following the same procedure as used in Mouton et al.⁴¹ for the simulation of LIF spectra at
287 low temperature. The global simulated LIF spectrum corresponds to the weighted sum of the
288 contributions of each individual species (PAHs and dimers of PAHs) according to this
289 formula:

$$290 \quad \text{Calculated Spectrum} \sim I_{laser} \cdot \sum_i (\theta_i \cdot \sigma_i(\lambda) \cdot N_i \cdot \text{Spectrum}(PAH_i, Dimers_i)) \quad (1)$$

291 where I_{laser} is the laser energy, θ_i the fluorescence quantum yield, $\sigma_i(\lambda)$ the
292 absorption cross section at the excitation wavelength λ , N_i the weight of the species (mainly
293 proportional to their concentrations) and $\text{Spectrum}(PAH_i, Dimers_i)$ the normalized emission
294 fluorescence spectrum of each considered PAH or dimer.

295 The contributions of the different PAHs and dimers are determined by adjusting their
296 relative concentration N_i until the best agreement is found between the experimental and the
297 global simulated spectrum. The fluorescence quantum yield θ_i has been considered constant
298 for all species because of the lack of knowledge concerning this data.

299 The reference papers from which the absorption and emission spectra of PAHs and
300 dimers of PAHs constituted the database are taken are reported in **table 2**. In order to be
301 consistent in terms of intensity and absorption lines positions, we only considered the
302 excitation spectra measured in solution by Karcher et al.^{29,37} to build the database of our
303 model. It would have been obviously more accurate to use PAH excitation spectra measured
304 at high temperature in the gas phase, but these data were only available for naphthalene⁴²,
305 pyrene⁴³ and anthracene⁴³ among the twenty PAHs included in our model. Hence, for the
306 sake of consistency, the use of these spectra would have required some corrections in
307 intensity to be comparable with the spectra measured in solution.

308 In comparison with the excitation spectra of PAHs, more data on the fluorescence
309 emission of PAHs at high temperature in the gas phase are available in the literature, notably

310 concerning the main PAHs in our model up to benzo(a)pyrene. As the fluorescence emission
311 spectra we used in our code required to be normalized in intensity, we chose to include in the
312 database PAH emission spectra measured at high temperature when they are available.

313 As stated above, spectra of selected PAH dimers have also been included in the
314 database. The spectroscopy of these species relies on the formation of PAH excimers from the
315 ground state dimers by the excitation of one of the two monomers ($M\cdots M$) into a first local
316 excitation (LE) state quickly followed by the stabilization of the excimer predominantly by
317 exciton resonance ($M^*M \leftrightarrow MM^*$) and/or by charge resonance interaction ($M^+M^- \leftrightarrow M^-M^+$)
318 ^{25,44,45}. Note that excitons and charge resonance interactions are responsible for the preferred
319 parallel arrangement of PAH excimers into stacked clusters that provide the smallest distance
320 between the molecular centers. The molecular rearrangement between the two minima of the
321 higher potential energy surfaces is shown in **fig.4**. The fluorescence emission of the excimer
322 is directly issued from this state and gives rise to the redshifted (in comparison with the
323 excitation wavelength), broad and unstructured fluorescence spectrum represented on the left
324 side of **fig.4**.

325 As shown in this figure, the excimer fluorescence depends on the binding energy (D_e)
326 as well as the repulsive energy of the ground state (depending on the intermolecular distance).
327 The maximum of the excimer fluorescence occurs from the bottom of the potential well of the
328 $(M-M)^*$ excimer to the ground state of the $M\cdots M$ dimer, whereas the emission at the smallest
329 and highest wavelength comes from the outer edges of the well. Since the repulsive potential
330 of PAH dimers remain poorly understood, we based our simulations on the following
331 consideration. We assumed that the binding energy can be defined as the difference between
332 the monomer and excimer fluorescence energy ²³. Hence, the energy bandwidth of the
333 excimer corresponds to the half width of the binding energy. As mentioned by Sumi ⁴⁶, a
334 fluorescence spectrum of an excimer in the liquid phase is a “*broad Gaussian-like band*”. A

335 similar shape is also observed in gas phase ²⁴. Consequently, excimer fluorescence spectra
336 have been fitted by a Gaussian function centered at the excimer energy provided by the
337 literature and characterized by a full width at half maximum (FWHM) equal to half of the
338 binding energy D_e . Fluorescence and binding energy of excimers are given in **table 3**. It is
339 worth noting that regardless the reference, the binding and excimer fluorescence energy are
340 relatively close to each other. For this reason, we used an averaged value for each excimer.

341 It is known from the literature that the excitation spectra of aromatic dimers resembles
342 monomers spectra ^{25,47}. They are only slightly shifted and broadened toward higher
343 wavelengths relative to the monomer absorption spectrum and have a longwave “trail” ⁴⁷. For
344 this reason, we considered in our model, for the UV excitation wavelengths, that the molar
345 extinction coefficients of the monomer were representative of the molar excitation
346 coefficients of the dimers. Concerning the visible excitation of the dimers, there is only very
347 little information available in the literature. However, it has been clearly highlighted that
348 dimers of PAHs as pyrene and perylene, which are both used in our simulation code, can
349 absorb at 488 and 532 nm and give rise to broad band emission fluorescence spectra in the
350 visible spectral region ³⁸. We considered an equal probability for their excitation in the visible
351 range (405, 488 and 532nm) for the five selected dimers. The intensities of the fluorescence
352 emission spectra were therefore only weighted by the adjusted value of the respective relative
353 concentrations N_i of each dimer.

354 From a numerical analysis point of view, at present we cannot rule out the existence of
355 multiple solutions of **equation 1**. Finding all the possible solutions that minimize the distance
356 between the measured fluorescence spectrum and the linear combination of PAHs/dimers
357 spectra within a certain residual is equivalent to estimating the number of local minima of an
358 unknown n-dimensional surface. In order to obtain a deep and reliable understanding of the
359 fluorescence emission in the visible, this is an important albeit not trivial challenge that will

360 be tackled in the future but currently goes beyond the scope of this paper. However, the
361 existence of multiple solutions does not affect the main conclusion of our investigation: there
362 are *no* linear combinations of the fluorescence spectra of twenty selected PAHs assumed to be
363 important soot precursors in the literature that can reproduce the experimentally observed
364 fluorescence emission in the visible. In turn, a handful of the fluorescence spectra of PAH
365 dimers are enough to result in (at least) one linear combination that very closely reproduces
366 the aforementioned fluorescence emission in the visible.

367 **3.3 Analysis of the fluorescence emission spectra**

368 Experimental and calculated spectra are reported in **fig. 5** and **fig. 6**. The red solid line
369 represents the experimental spectra, while the blue solid line corresponds to the global
370 calculated spectrum, sum of the individual contributions of PAHs (thin colored solid lines)
371 and dimers (thin colored dashed lines).

372

373 ***3.3.1 Fluorescence induced by 213.5 and 282 nm excitation wavelengths***

374 At both UV excitation wavelengths, the excellent match of experimental and
375 calculated spectra shows that the UV fluorescence emission (300-450 nm) comes from the
376 fluorescence of PAH monomers. This spectral feature is mainly constituted of the spectral
377 contributions of naphthalene, pyrene and fluoranthene, which all possess strong oscillator
378 strengths at both excitation wavelengths. The contributions of fluorene, anthracene,
379 phenanthrene are also noticeable below 20 mm HAB, while the contributions of
380 benzo(a)pyrene, perylene and benzo(ghi)perylene appear higher in the flame. It is worth
381 noting that only nine over the twenty available PAHs in our database are necessary to
382 correctly reproduce the UV part of the fluorescence spectra, and this further strengthens the
383 observation that multiple linear combinations of PAHs spectra may lead to simulated spectra
384 very similar to the experimental spectrum.

385 Above 15 mm HAB, we observe the emergence of a contribution in the visible region
386 beyond 500 nm that cannot be reproduced by any combination of the PAH monomers spectra
387 in our database. To correctly reproduce the entire experimental spectra, an additional
388 contribution coming from three dimers of PAHs (pyrene, benzo(a)pyrene, perylene) is
389 required (**fig. 5**). This addition leads to an excellent agreement with the experimental spectra
390 all along the flame height, showing that the visible part of the emission spectra can only
391 derive from dimers of moderate-sized PAHs and not from large PAHs. This clearly means
392 that the common interpretation correlating the visible emission of such spectra measured in
393 flames to the fluorescence of different classes of large PAHs is not adequate and leads to
394 flawed conclusions. Moreover, we show here that, with the only exception of naphthalene, the
395 strong overlap of the different spectral contributions of the excited PAHs prevents any precise
396 distinction of classes of PAHs based on the fluorescence wavelength range.

397

398 ***3.3.2 Fluorescence induced by 405 nm excitation wavelength***

399 Only three PAHs (fluoranthene, benzo(a)pyrene and perylene) out of the twenty in our
400 database possess strong enough absorption bands to be excited at 405 nm. Fluoranthene
401 spectroscopy features an anomalous broadband excitation spectrum⁴⁸ strongly red-shifted in
402 comparison to PAHs of the same size (peak emission at 450 nm against 390 nm for pyrene).
403 The experimental and simulated spectra obtained at 405 nm excitation wavelength are shown
404 in the left column of **fig. 6**. The spectral analysis reveals that the structure of the experimental
405 spectra is well reproduced by the contributions of fluoranthene, benzo(a)pyrene and perylene
406 at low HAB, while supplementary contributions of dimers of pyrene, benzo(a)pyrene and
407 perylene are required higher in the flame. The increase of the excitation wavelength from the
408 UV range to 405 nm clearly limits the pool of excitable PAHs and constitutes an experimental
409 approach to selectively excite the largest PAHs formed in the flame. Moreover, it implicitly

410 underlines the formation of dimers of PAHs which, as for UV excitation, strongly contributes
411 to the visible part of the measured fluorescence emission spectra.

412

413 ***3.3.3 Fluorescence induced by 488 and 532 nm excitation wavelengths***

414 The fluorescence spectra shown in the last two columns in **fig. 6** are obtained with
415 visible excitations (488 and 532 nm wavelength, respectively). As shown in the figure, there
416 is no spectral evolution of the global emission structure against HAB in strong contrast with
417 the spectra recorded with UV excitations. Here, the spectra feature intense Stokes and anti-
418 Stokes components from both sides of the excitation wavelength. No PAHs can be excited
419 anymore at these wavelengths and the simulated spectra involve only dimers of PAHs. In
420 particular, an excellent agreement between the simulations and the experimental spectra
421 acquired at 488 nm excitation wavelength is obtained at any HAB with the dimer of
422 benzo(a)pyrene and a smaller contribution from the dimer of pyrene and perylene. The
423 simulation of the spectral structure measured at 532 nm, requiring the contribution
424 benzo(a)pyrene and perylene, is also satisfying, except for the edges near 700 nm. This
425 discrepancy may be attributed to the limited number of dimers in our database. The overall fit
426 highlights that the spectral shift of the maximum intensity of the spectra from 510 to 560 nm,
427 is due to a more efficient excitation of the dimer of perylene at 532 nm in comparison to the
428 excitation at 488 nm.

429

430 **3.4 Effect of the delay on the recorded LIF spectra**

431 Another strong argument for dimers optical detection in flames relies on the
432 fluorescence lifetimes of the excited species. It is known that dimers of PAHs have
433 substantially longer fluorescence lifetimes than PAH monomers^{44,49}, which can be
434 highlighted by delaying the detection gate width of the fluorescence signals. In order to

435 strengthen the evidence of dimer formation in the sooting flame, we carried out a series of
436 LIF measurements in which we varied the gate delay (GD) of the ICCD camera with respect
437 to the peak of the temporal LIF signal, considered to be the prompt fluorescence in this case.
438 All the delayed LIF spectra have been recorded with the same 40 ns gate width, but
439 temporally shifted in order to observe the species with longer τ . **Fig. 7** shows the LIF spectra
440 measured at 60 mm HAB at 213.5 nm excitation wavelength and for different GD values.

441 We have shown above that PAHs and dimers of PAHs can be excited at 213.5 nm and
442 fluoresce in two different spectral ranges. From our database, it appears clearly that PAHs
443 mainly fluoresce in the spectral range 300-450 nm, while dimers of PAHs feature strong
444 fluorescence bands in the spectral range 400-700 nm. In **fig. 7**, we show that two different
445 spectral contributions can be distinguished according to the GD. The UV part of the spectrum,
446 characteristic of the PAHs fluorescence spectral range, is indeed strongly reduced with a late
447 detection while the LIF delayed detection temporally favors the red-shifted LIF signal coming
448 from the excited dimers. Note that the measured fluorescence spectra remain unchanged when
449 $GD > 5$ ns, featuring a very short fluorescence decay time for the PAHs in flames as already
450 observed in the literature ⁵⁰. We also performed the same experiments with a visible
451 excitation wavelength at 488 nm. In this case, not reported here, we did not observe any
452 change in the shape of the LIF spectra regardless of the time delay. This observation clearly
453 denotes the excitation at visible wavelength of a same sort of species characterized by
454 fluorescence spectra pointing to the fluorescence of dimers of PAHs.

455 As we have shown above, the contributions of PAHs and dimers of PAHs to the global
456 fluorescence spectrum evolve with the HAB. We also performed delayed experiments at
457 different HAB. In **fig. 8**, we report a comparison of three LIF spectra, measured at 213.5 nm
458 excitation wavelength with and without applying a delayed detection of 10 ns for three
459 different HAB.

460 At 30 mm HAB, the important contribution to the UV region of the spectrum
461 disappears by delaying the detection, confirming the simultaneous important presence of
462 PAHs and dimers of PAHs in this zone of the flame. The impact of the delayed detection on
463 the measured spectrum is slightly reduced at higher HAB due to the smaller contribution of
464 the PAHs fluorescence to the global spectrum. However, this systematic depletion provides
465 another indication that PAHs contribute to the fluorescence spectra in the spectral range 300-
466 450 nm up to 60 mm HAB, consistent with the spectral analysis provided in the main text.
467 Note that we also carried out similar experiments with visible excitations wavelengths at 488
468 nm and 532 nm. In this case, no spectral change of the emission spectrum was observed at
469 any HAB. Here, this observation is characteristic of the only excitation of dimers of PAHs
470 with visible laser wavelengths.

471 As expected from their spectroscopic properties³⁸ and confirmed by this work, dimers
472 of PAHs can be excited both in the UV and the visible range. This property can be highlighted
473 by comparing the fluorescence spectra obtained for different excitation wavelengths. In **fig.9**,
474 we show a comparison between two prompt fluorescence spectra recorded at 488 and 532 nm
475 excitation wavelength and one fluorescence spectrum obtained at 213.5 nm excitation
476 wavelength and temporally delayed to exclude PAHs fluorescence emission. From this figure,
477 it appears that these spectra are characterized by a similar broadband and structureless spectral
478 shape, only slightly red-shifted according the excitation wavelength from the UV to visible.
479 The slight shift between the different spectra can be attributed, as highlighted with our model,
480 to the fluorescence of different dimers of PAHs, the intensities of which may be favored by
481 the choice of the excitation wavelength, or by changes of their emission properties with the
482 excitation wavelength as proposed elsewhere³⁸.

483

484 **3.5 Implications for soot formation**

485 The detailed analysis of the fluorescence spectra of the sooting flame enables to
486 clearly attribute the measured intense visible LIF signal to the spectral signature of dimers of
487 moderate-sized PAHs. Moreover, we show that the contributions of several dimers are
488 necessary to properly reproduce the experimental spectra. **Fig. 10** shows the relative evolution
489 against the flame HAB of the normalized LIF signals of the main PAHs and dimers of PAHs,
490 corresponding to the maximum LIF intensities determined for each species from the simulated
491 spectra of **fig. 5** and **fig. 6**. The dimer profile corresponds to an average profile of all the
492 PAHs dimers as their shapes are very similar regardless of the dimers. The relative soot
493 volume fraction profile (black line), previously measured³³ by laser induced incandescence
494 (LII), is also shown in **fig. 10**. These data highlight that the formation of the dimers starts
495 slightly above the formation of PAHs (around 20 mm HAB) and reaches a maximum around
496 60 mm HAB, which corresponds to the beginning of the soot inception region. Consumption
497 of dimers corresponds to the formation of soot particles, which ends when the pool of dimers
498 has been fully consumed.

499 These results consequently support the hypothesis of kinetic rather than
500 thermodynamic control frequently used in emerging soot formation mechanisms^{15,19-21}. For
501 instance Eaves et al.^{15,19} introduced in their models the concept of the reversibility of the
502 nucleation, implying that nucleation may not be governed by equilibrium processes as already
503 suggested by the pioneering work of Dobbins et al.⁵¹. In this framework, the formation of
504 dimers of moderate-sized PAHs is still a reversible process, however nucleation requires the
505 dimers stabilization by the formation of a strong chemical bond as also proposed by Kholghy
506 et al.²¹ through a sequence of hydrogen abstraction and carbon-carbon bond formation or
507 dehydrogenation.

508 Another hypothesis to explain the stabilization of PAH dimers in flames proposes the
509 formation of aliphatic bridges between two PAHs. This suggestion is supported with

510 experimental results in the recent work of Adamson et al.⁵², in which they detected and
511 identified aliphatically bridged PAHs in an ethylene/O₂ coflow diffusion flame with a tandem
512 mass spectrometer. Although the geometrical arrangement of the two bridged PAHs could not
513 be determined in the work of Adamson et al.⁵² we believe that these species might as well
514 correspond to the same species fluorescing in the visible domain and observe by LIF in our
515 work. The PAHs connected by a short carbon chain form a stable intramolecular PAH dimer
516 involving the two bridged PAHs into a parallel arrangement involving van der Waals forces.
517 Under this configurations, such intramolecular dimers have been shown to provide similar
518 spectral signatures under laser excitation as intermolecular PAH dimers⁴⁵ (dimers only
519 connected by van der Waals forces). Whether aliphatic bridged PAHs are formed in flames,
520 they probably rearrange themselves into intramolecular PAHs dimers, the dimerization
521 process being facilitated by the carbon chain connecting the two monomers. Alternatively,
522 intermolecular dimers of PAHs could also be first formed and stabilized by the formation of
523 an aliphatic chain instead of a simple carbon bond as envisaged by Kholghy et al.²¹, between
524 the two PAHs according to a similar irreversible process as proposed by this group²¹.

525 It is clearly beyond the scope of this work to discuss the detailed kinetics leading to
526 the formation of these dimers, the main objective of this paper being to bring experimental
527 evidence supporting the formation of dimers of PAHs in a methane diffusion flame. However,
528 the formation of strong carbon bonds between two PAHs is likely a required step to stabilize
529 the dimer and initiate the process of nucleation. According to our experiments, we cannot
530 state if these chemical bonds are formed after the dimers as proposed by Eaves et al.¹⁹ or
531 Kholghy et al.²¹, or before according to the hypothesis of aliphatic bridges. However, all
532 these results clearly point to the dimers of moderate-sized PAHs being the elemental building
533 blocks in the soot nucleation process.

534

535 **4. Conclusion**

536 In this work, we carried out the experimental study of a laminar diffusion sooting flame
537 of methane by laser induced fluorescence (LIF). A large database of emission fluorescence
538 spectra has been recorded at different HAB along the vertical centerline of the flame and for
539 different UV and visible excitation wavelengths. The analysis of these spectra has been
540 performed by the use of a simple model relying on a spectroscopic database containing the
541 excitation and emission fluorescence spectra of twenty pericondensed PAHs and five dimers
542 of PAHs. From the analysis of the spectra provided by the comparison of the experimental
543 and simulated spectra, we clearly distinguished two main contributions in the emission
544 spectra. The first contribution, dominant for the first HAB and ranging from 300 to 450 nm, is
545 undoubtedly attributed to the fluorescence of some specific PAHs from naphthalene to
546 benzo(ghi)perylene. By contrast, we showed that the second contribution, occurring for higher
547 HAB in the flame and characterized by an intense and unstructured emission spectra at 400-
548 700 nm, could not be reproduced by any combination of PAHs spectra. Based on
549 spectroscopic considerations, it turns out that this second contribution is very likely
550 characteristic of the emission of moderate-sized dimers of PAHs.

551 The analysis of the measured spectra clearly supports the formation of dimers of
552 moderate sized PAHs in the inception region of a sooting flame, very likely meaning that
553 these species play a significant role in the soot nucleation process. These results are consistent
554 with recent kinetic models that consider dimers as an intermediate species conditioning the
555 transition to soot particles ^{19,21}. It is currently not clear if dimers could be extracted from
556 flames with typical methods commonly used for flame investigations (as molecular beam
557 mass spectrometry for instance). Indeed, due to their brief lifetime and poor thermodynamic
558 stability, this certainly represents a challenging task and laser diagnostic might be the most
559 suitable choice to characterize these species.

560 However, depending on the structure of the dimers, notably the presence of a strong
561 chemical bond between the two monomers, there might be some opportunities to extract these
562 species or to study them indirectly. In this case, it is probable that the parallel arrangement of
563 the dimer structure due to van der Waals forces could not be preserved and the sampled
564 species might therefore correspond to the species identified by Adamson et al.⁵².

565 Surely, much work remains to be done to determine the exact nature of these species
566 and the mechanisms involved in the nucleation step. Nevertheless, the analysis we provided
567 sheds new light on the soot nucleation. The very existence of dimers of moderate-sized PAHs
568 in the nucleation region of sooting flames is strong evidence that soot nucleation is kinetically
569 rather than thermodynamically controlled, which is valuable information for the advancement
570 of modeling and the understanding of the soot formation process at its fundamental level.

571 **Conflicts of interest**

572 There are no conflicts of interest

573

574 **Acknowledgements:**

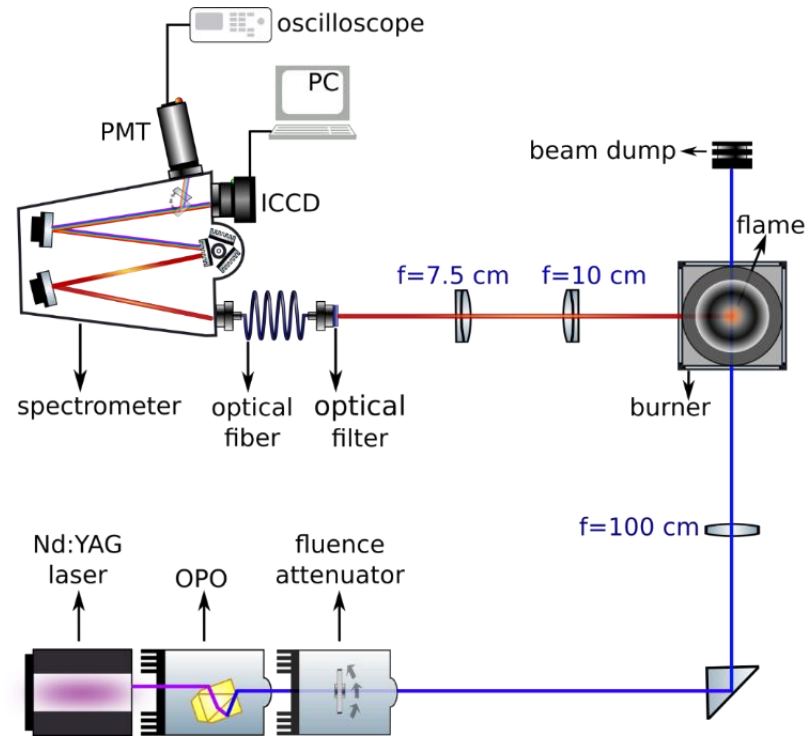
575 This work was supported by the Agence Nationale de la Recherche through the LABEX
576 CAPPA (ANR-11-LABX-0005), the Région Hauts-de-France, the Ministère de
577 l'Enseignement Supérieur et de la Recherche (CPER Climibio) and the European Fund for
578 Regional Economic Development.

579

Figures, Tables and Captions

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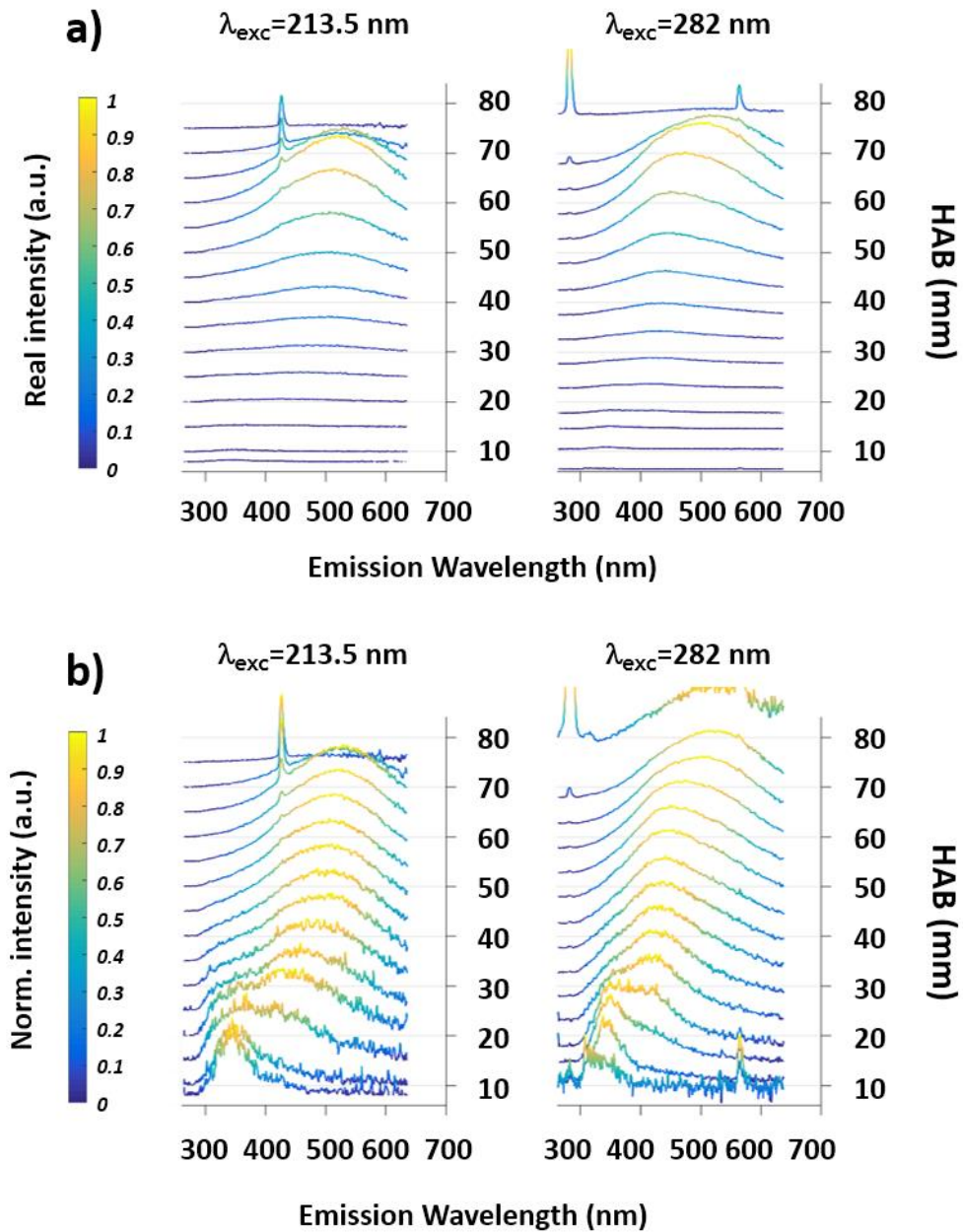
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Figure 1: Experimental configuration for the LIF measurements.

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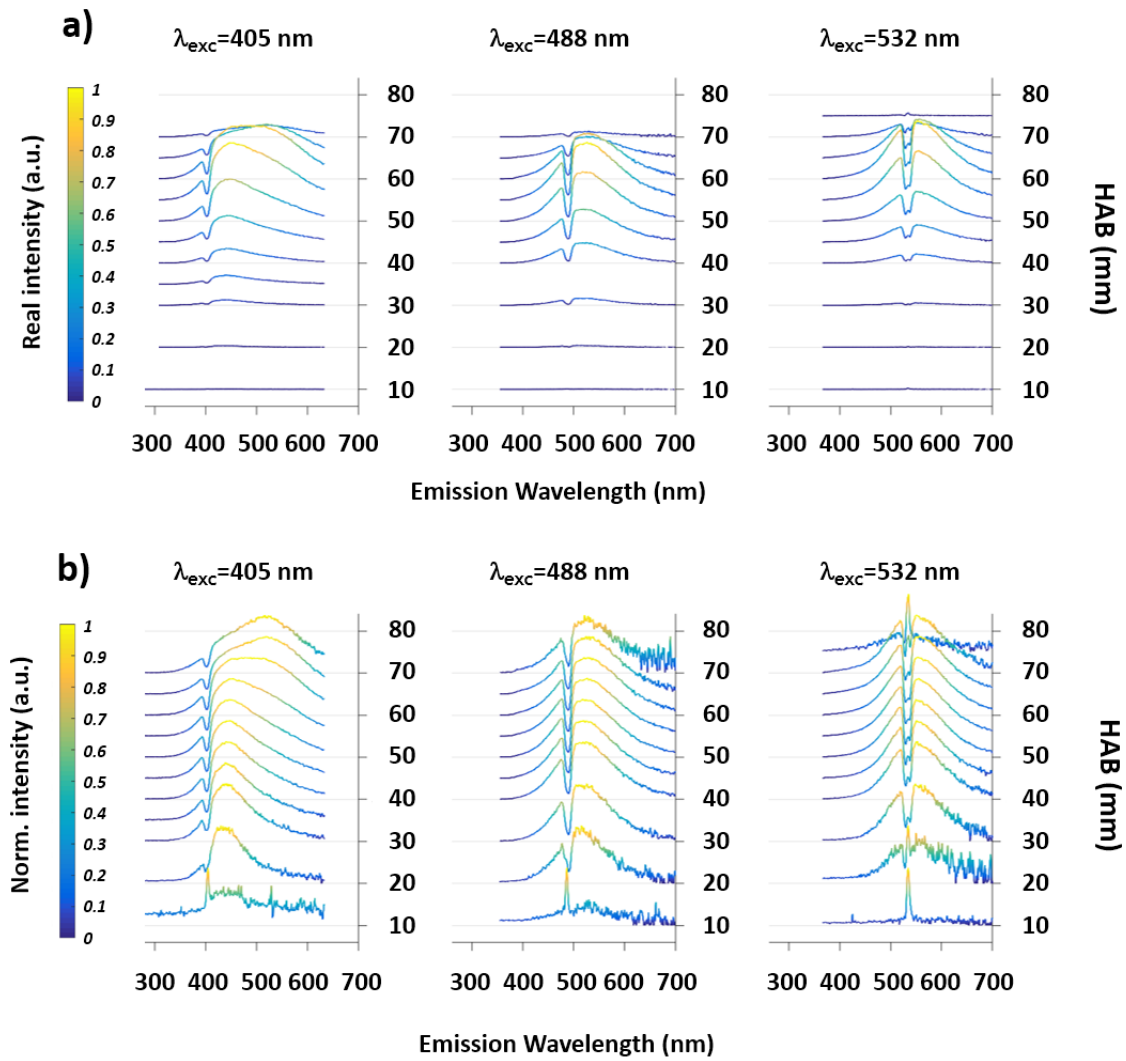
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Figure 2: Fluorescence emission spectra recorded along the vertical centerline of the flame
 588 for two UV excitation wavelengths. a) Raw intensity (a.u.) b) Normalized intensity (a.u.)

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The peaks around 427 nm and 564 nm correspond to the 2nd emission order of the grating for
 590 the laser excitation wavelengths.

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Figure 3: Fluorescence emission spectra recorded along the vertical centerline of the flame

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for three visible excitation wavelengths. a) Raw intensity (a.u.) b) Normalized intensity (a.u.). The

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strong absorption features is due to notch filters used to suppress laser diffusion during the

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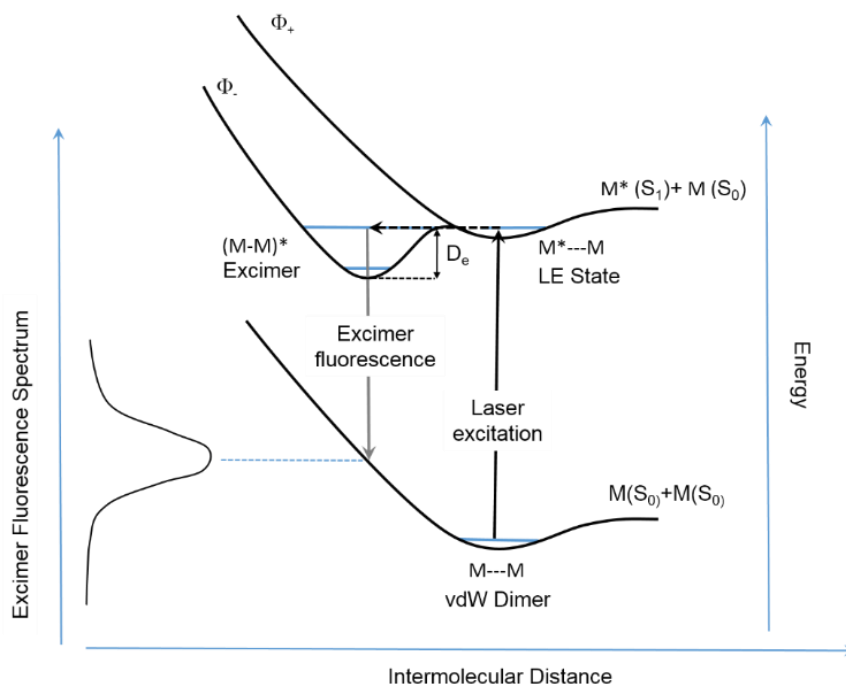
experiments.

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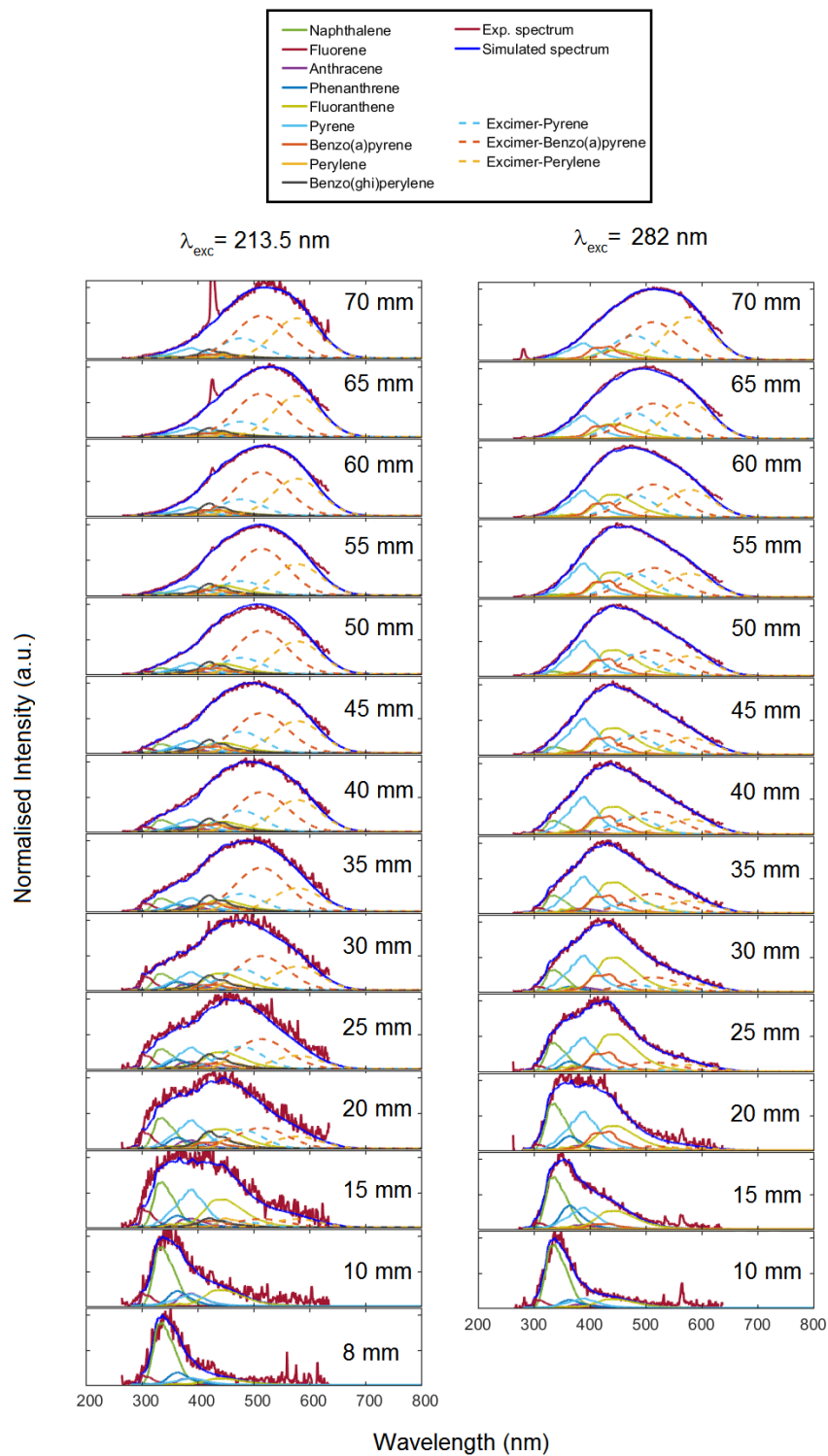
Figure 4: Schematic potential energy diagram for an excimer formation $(M-M)^*$ via the excitation of the ground state van der Waals (vdW) dimers $M\cdots M$ constituted by two monomers M ²⁵

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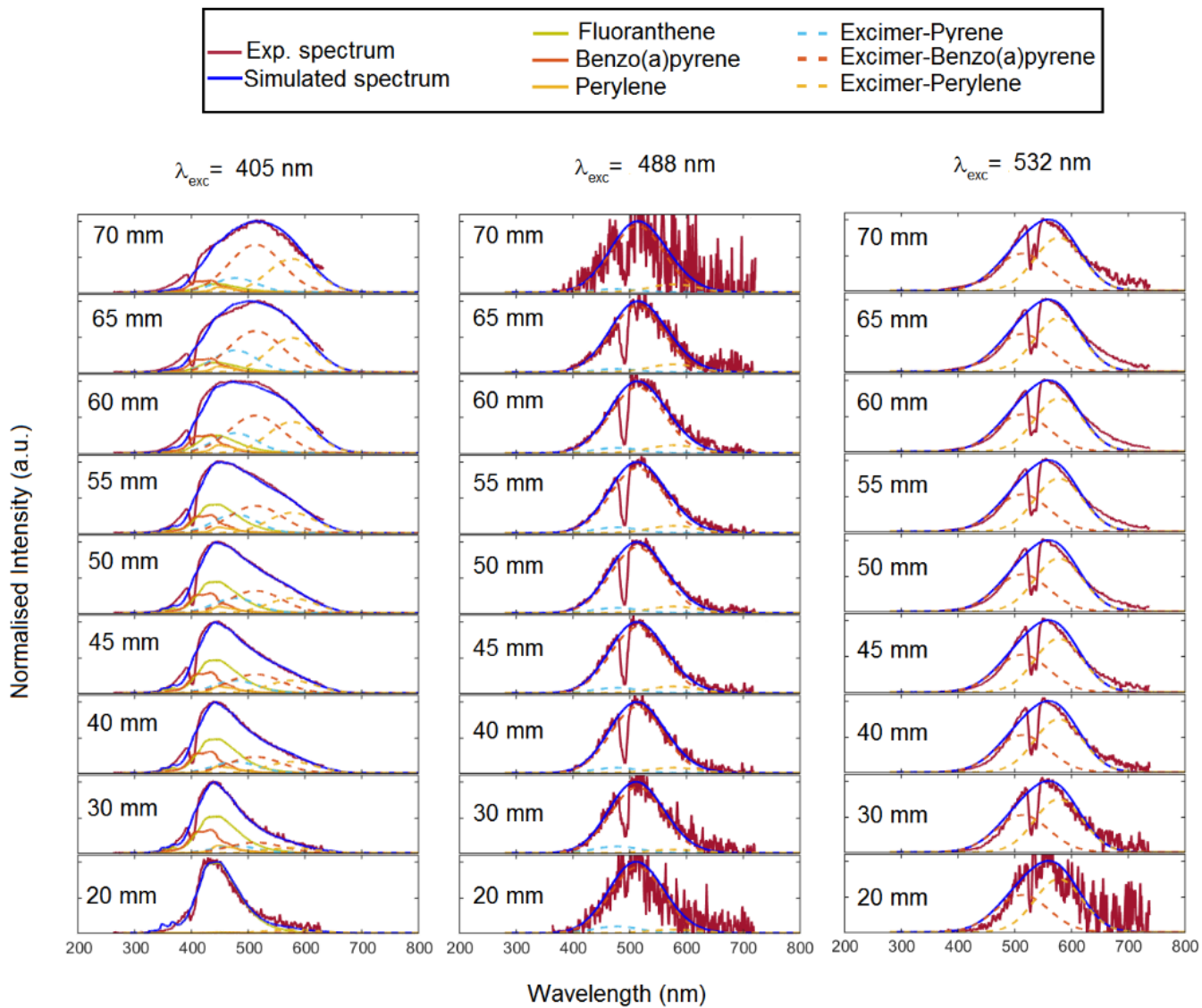


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608 **Figure 5:** Calculated and experimental fluorescence emission spectra obtained for different UV

609 excitation wavelengths along the vertical centerline of the flame against HAB

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612 **Figure 6:** Calculated and experimental fluorescence emission spectra obtained for different visible

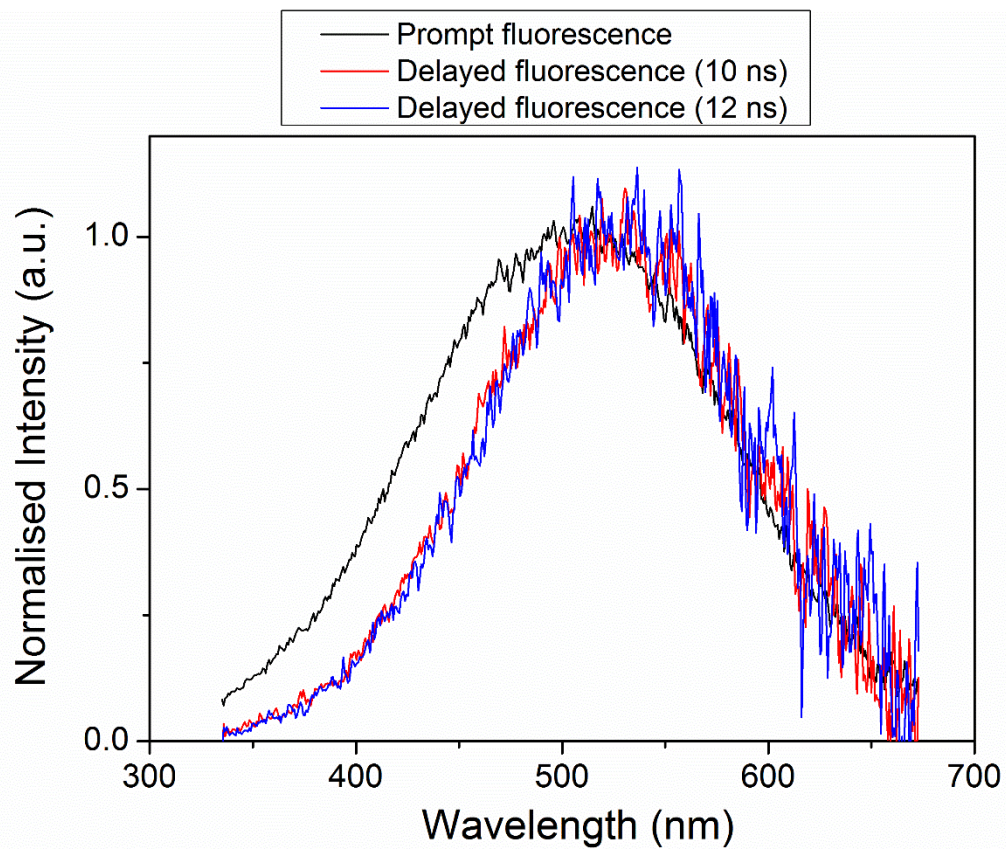
613 excitation wavelengths along the vertical centerline of the flame against HAB.

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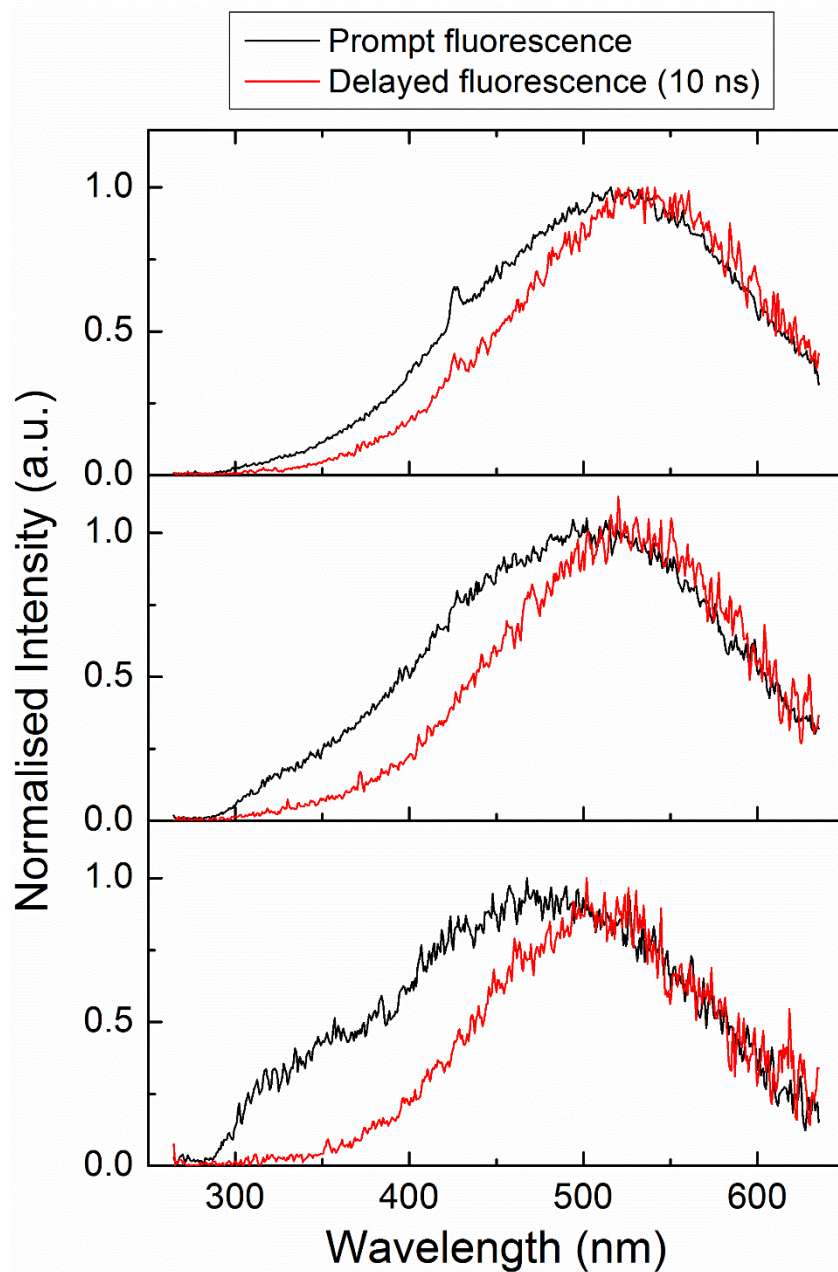
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620 **Figure 7:** Prompt and delayed fluorescence spectra measured at 60 mm HAB, at 213.5 nm

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excitation wavelength.

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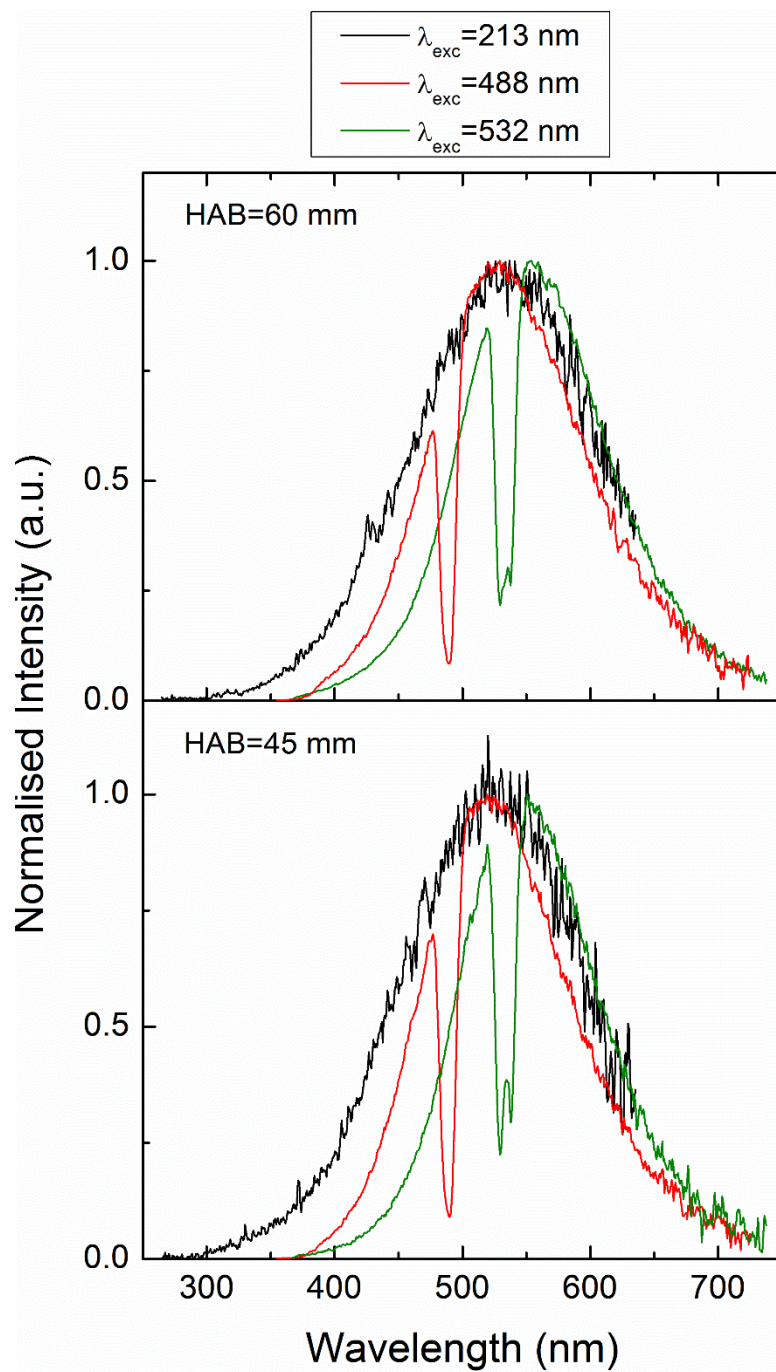
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Figure 8: Comparison between prompt and delayed fluorescence spectra at 213.5 nm

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excitation wavelength for three selected HAB.



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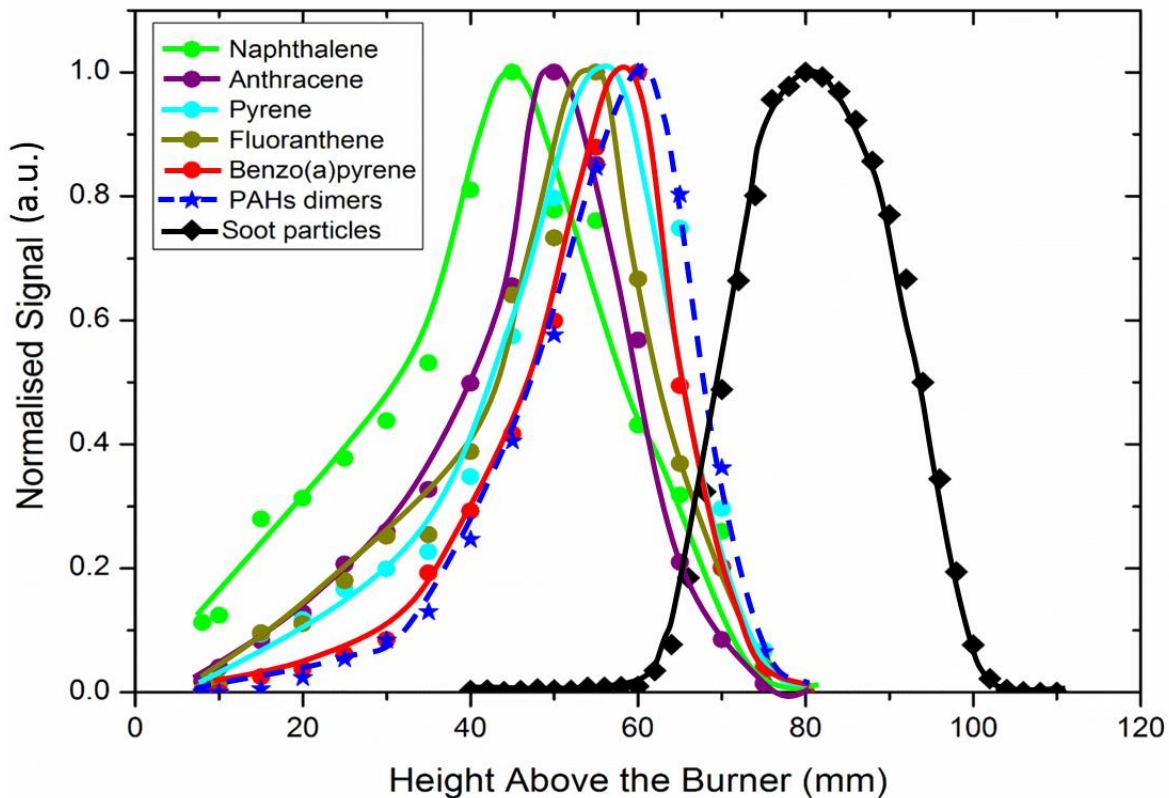
627 **Figure 9:** Comparison between delayed fluorescence spectra at 45 and 60 mm for 213.5, and

628 prompt fluorescence spectra obtained upon 488 and 532 nm excitation wavelength

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633 **Figure 10:** Specific profiles of PAHs and dimers subtracted from the LIF intensities determined from
 634 the simulated spectra obtained along the centerline of the flame. The dimers profile is an average
 635 profile of the dimers profile of pyrene, benzo(a)pyrene and perylene. The soot profile has been
 636 obtained with laser induced incandescence (LII)

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PAHs					
2-rings	3-rings	4-rings	5-rings	6-rings	7-rings
Naphthalene	Anthracene Fluorene Phenanthrene	Fluoranthene Pyrene Chrysene Naphhtacene	Benzo(a)pyrene Benzo(e)pyrene Perylene Benzo(ghi)perylene Benzo(ghi)fluoranthene Benzochrysene Benzo(c)chrysene Dibenzo(ac)anthracene Dibenzo(ah)anthracene	Anthanthrene Indeno(1,2,3-cd)pyrene	Coronene
DIMERS of PAHs					
2-rings	3-rings	4-rings	5-rings		
	Anthracene	Pyrene	Benzo(a)pyrene Perylene Benzo(ghi)perylene		

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Table 1: PAHs and dimers included in the model for the simulation of the spectra.

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PAHs	Absorption Spectra	Emission Spectra
Naphthalene	Karcher et al. ²⁹	Orain et al. ⁵³
Fluorene	Karcher et al. ²⁹	Karcher et al. ²⁹
Anthracene	Karcher et al. ³⁷	Cignoli et al. ⁵⁴
Phenanthrene	Karcher et al. ³⁷	Cignoli et al. ⁵⁴
Fluoranthene	Karcher et al. ³⁷	Ledier ⁵⁵
Pyrene	Karcher et al. ³⁷	Cignoli et al. ⁵⁴
Chrysene	Karcher et al. ³⁷	Kirsch et al. ⁵⁶
Naphthacene	Karcher et al. ²⁹	Karcher et al. ²⁹
Perylene	Karcher et al. ²⁹	Cignoli et al. ⁵⁴
Benzo(ghi)perylene	Karcher et al. ³⁷	Cignoli et al. ⁵⁴
Benzo(a)pyrene	Karcher et al. ³⁷	Cignoli et al. ⁵⁴
Benzo(e)pyrene	Karcher et al. ³⁷	Karcher et al. ³⁷
Benzo(ghi)fluoranthene	Karcher et al. ³⁷	Karcher et al. ³⁷
Benzo(b)chrysene	Karcher et al. ³⁷	Karcher et al. ³⁷
Benzo(c)chrysene	Karcher et al. ³⁷	Karcher et al. ³⁷
Dibenzo(ac)anthracene	Karcher et al. ³⁷	Karcher et al. ³⁷
Dibenzo(ah)anthracene	Karcher et al. ³⁷	Karcher et al. ³⁷
Coronene	Karcher et al. ²⁹	Cignoli et al. ⁵⁴
Anthanthrene	Karcher et al. ³⁷	Karcher et al. ³⁷
Indeno(1,2,3-cd)pyrene	Karcher et al. ³⁷	Karcher et al. ³⁷

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Table 2: The corresponding references for the absorption and emission spectra used in our model.

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Excimer	Excimer Peak Fluorescence (cm ⁻¹)	Binding Energy D _e (cm ⁻¹)
Anthracene	22220 ^a	2200 ^a
Pyrene	20920 ^b 20530 ^c 20750 ^d	6890 ^b 6350 ^c 6130 ^d 5860 ^e
Benzo(a)pyrene	19460 ^b	8040 ^b 5360 ^d
Perylene	17300 ^b	5750 ^b
Benzo(ghi)perylene	19840 ^d	6060 ^b 6850 ^d

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Table. 3: Fluorescence and binding energy of several excimers.

(a) Chakraborty et al. ⁵⁷, (b) Azumi et al. ⁴⁹, (c) Birks et al. ⁵⁸,

(d) Birks et al. ⁵⁹, (e) Birks et al. ⁶⁰

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