Journal of Photochemistry and Photobiology A: Chemistry 315 (2016) 87–93

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Computational assessment of the fluorescence emission of phenol oligomers: A possible insight into the fluorescence properties of humic-like substances (HULIS)

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ARTICLE INFO

Article history:
Received 14 July 2015
Received in revised form 21 September 2015
Accepted 22 September 2015
Available online 26 September 2015

Keywords:
Atmospheric photochemistry
Oligomeric compounds
Excitation–emission fluorescence matrix
Phototransformation
Density functional theory

ABSTRACT

Compounds with fluorescence in the humic-like substances (HULIS) region are known to be formed under conditions where the oxidation (which could lead to the oligomerization) of phenolic compounds is operational, because of the formation of phenoxy radicals. However, there was no evidence to date that such fluorescence emission was really due to phenol oligomers. In this work, the fluorescence of phenol and some of its oligomers was studied by computational methods and it was compared with experimental data, when allowed by the availability of commercial standards. The oligomer fluorescence depends on the contribution of different stable conformers, which differ from one another for the dihedral angles between the aromatic rings. Differences in the dihedral angles are also observed between the ground states and the corresponding excited singlet states. The predicted wavelengths of fluorescence emission increase with increasing the number of aromatic rings, up to a plateau at around 450 nm. Compounds with more than three-four aromatic rings are not expected to show emission in a different range, because the transitions causing fluorescence involve only three consecutive rings. These results support the hypothesis that oligomers account for the fluorescence emission in the HULIS region, which has been observed under the photochemical and photosensitized transformation of phenolic compounds.

1. Introduction

Humic-like substances (HULIS) are important components of the atmospheric aerosols, of which they affect for instance the ability to nucleate water droplets and to absorb sunlight [1–3]. HULIS share some common features with humic and fulvic acids found in surface waters and soils (such as for instance the optical properties), but they are much smaller than humic acids and possess a smaller fraction of aromatic moieties and a larger fraction of aliphatic ones [4]. HULIS account for an important part of the water-soluble organic carbon in atmospheric aerosols, and they are thought to originate from both primary (biomass burning, release of organic compounds from water and soil to the atmosphere) and secondary processes (atmospheric reactions) [5–12].

The characterization of HULIS has been carried out with different techniques, including mass spectrometry, IR and NMR spectroscopy [13–16]. Unfortunately, these techniques often require sample fractionation and enrichment steps that would be problematic for a routine analysis of atmospheric samples. In contrast, characterization by absorption and fluorescence spectroscopy allows information to be obtained with minimal sample pre-treatment [17,18].

Several potential processes that could generate HULIS have been studied in the laboratory. Among these, photochemical reactions involving phenolic compounds in the presence of triplet sensitizers produce species with many similarities (functional groups, absorption and fluorescence spectra, hygroscopic properties) to atmospheric HULIS [19–23]. Interestingly, the same processes induce phenol oligomerization through the corresponding phenoxy radicals [19,23–25]. Phenol oligomers might or might not account for the observed properties, because additional compounds would also be formed under the same conditions. However, phenols and HULIS emit in clearly separated wavelength intervals [17,26,27], and the photochemical and photosensitized

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http://dx.doi.org/10.1016/j.jphotochem.2015.09.012

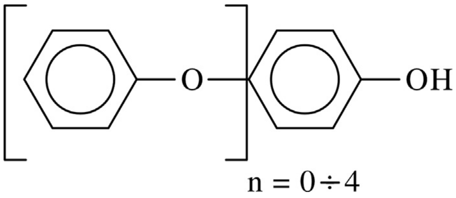
transformation of phenols produces a gradual shift of the fluorescence emission range towards the HULIS region [23].

The testing of the hypothesis that the fluorescence in the HULIS region is accounted for by phenol oligomers (trimers, tetramers and so on) has to face the difficulty that these compounds are hardly available as commercial standards. To by-pass this problem, the present work carries out a quantum mechanical assessment of the fluorescence emission of phenol and of some of its oligomers, optimizing and validating the computational techniques by comparison with the available experimental data. By so doing, one can predict the fluorescence behavior of compounds for which standards are not available, and carry out a comparison with the known HULIS emission.

2. Materials and methods

The absorption spectra were measured with a Varian Cary 100 Scan UV–vis double-beam spectrophotometer, using quartz cuvettes (1.000 cm optical path length). The excitation-emission matrix (EEM) fluorescence spectra were taken with a VARIAN Cary Eclipse Fluorescence Spectrophotometer, with an excitation range from 200 to 400 nm at 10 nm steps, and an emission range from 200 to 600 nm with a scan rate of 1200 nm min^{-1}. Excitation and emission slits were set at 5 nm for 0.1 mM phenol (Aldrich, 99% purity grade) and at 20 nm for 0.1 mM 4-phenoxyphenol (Aldrich, 99%). Spectra were taken in a fluorescence quartz cuvette (Hellma) with 1.000 cm optical path length. The Raman signal of water was taken as a reference for lamp intensity and signal stability within different measurements.

The computational study was performed within the Density Functional Theory (DFT) [28–30] with the following procedure: we first optimized the geometries of the ground states, then we calculated the excitation energies with the Time-Dependent DFT (TD-DFT) [31,32]. This method provides a reasonable accuracy at reasonable computational costs (time and computing resources) [33–35]. The excitation energies calculated in this way correspond to the maxima in the absorption spectra, as this approach does not include vibrational contributions or dynamic solvent effects. Actually, our intent is not to fully reproduce the experimental absorption spectra, but only to identify the most important transitions and reproduce the fluorescence spectra. When more conformations are possible for a certain molecule, each set of transitions is reported scaled by the weight of the corresponding conformation (see details in the Supplementary Material, hereafter SM). In the following, each molecule was re-optimized in its first excited state, and the difference between its energy and the one calculated for the ground state at the excited state geometry was taken as emission (fluorescence) energy. Solvent effects (water) to the electronic energies were introduced both in geometry optimization and TD-DFT calculations by the Polarized Continuum Method (PCM) [36,37] within the universal Solvation Model Density [38,39]. There exist a wide variety of DFT functionals used in conjunction with the Time-Dependent approach. Therefore, a preliminary screening work was carried out and 17 different functionals were tested (see details in the SM). After the screening, we decided to use the mPWLYP functional (modified Perdew–Wang exchange functional) [40] and Lee–Yang–Parr correlation [41,42] with the Pople basis set 6-31 + G(d) [43,44], because this method gives a suitable approximation of the experimental values and requests reasonable calculation time. Calculations were performed by the quantum package Gaussian 09-A [45]. Figs. 2 and 7 and Figs. SM1–SM7 (SM) and the figures embedded in tables in the SM were obtained with the graphical program Molden [46]. Fig. 7 and Figs. SM2, SM4, SM6, SM7 in the SM show the differential electronic density maps at the excited state geometries in the electronic excitation, *i.e.* the graphic representation of the difference in electronic densities between the ground and the first excited state responsible for the fluorescence. In other terms, the red areas are where the electron comes from, while the blue area is where the electron goes (these areas roughly correspond to HOMO and LUMO in HOMO–LUMO dominated electronic transitions, as it is the case here).



Scheme 1. The poly-*para*-phenoxyphenols studied.

3. Results and discussion

The absorption and fluorescence properties were calculated for a series of poly-*para*-phenoxyphenols (Scheme 1): phenol, 4-phenoxyphenol (4PP), 4-(4-phenoxy)phenoxyphenol (4PPP) and 4-(4-(4-phenoxy)phenoxy)phenoxyphenol (4PPPP). For phenol and 4PP, the predictions of calculations were compared with the available experimental data. To confirm the predicted trend of the fluorescence emission wavelengths, partial calculations were also carried out for a 5-ring system (the latter calculations were

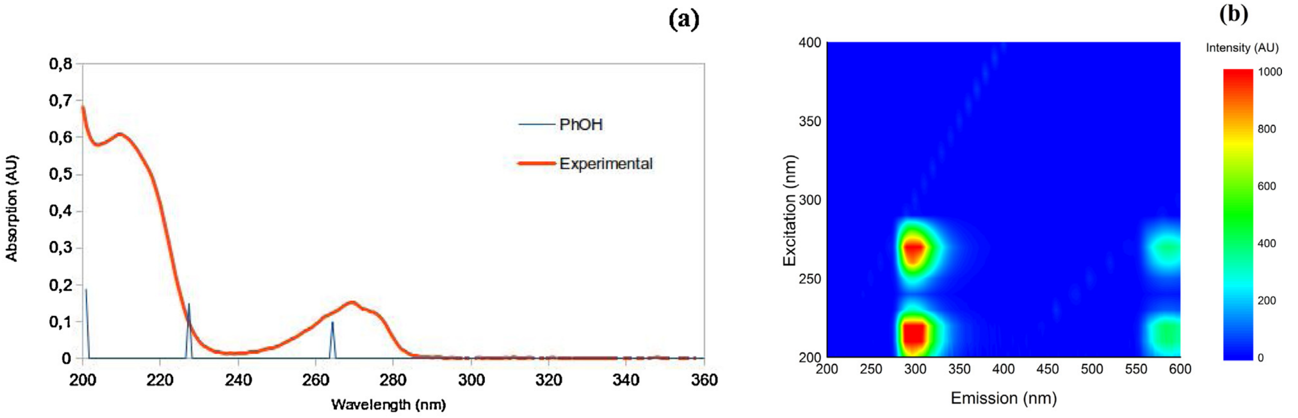


Fig. 1. (a) Experimental absorption spectrum of 0.1 mM phenol and calculated transitions (AU = absorbance units). (b) EEM matrix of 0.1 mM phenol in aqueous solution.