Pyrene and its selected 1-substituted derivatives revisited: A combined spectroscopic and computational investigation

Hümeyra Örücü [a], Nursel Acar [b], *

[a] Department of Physics, Faculty of Science, Ege University, 35100 Bornova / İzmir, Turkey
[b] Department of Chemistry, Faculty of Science, Ege University, 35100 Bornova / İzmir, Turkey

ABSTRACT

Pyrene and its $-OH$, $-NH_2$, and $-CN$ substituted derivatives were investigated experimentally by using UV/Vis absorption spectroscopy, steady state and time-resolved fluorescence spectroscopy in different polarity solvents. The computational part includes investigation of Pyrene and derivatives in excited S_1 state in gas phase and in solution. Calculations were carried out with density functional theory (DFT) and time-dependent density functional theory (TDDFT) at B3LYP/6-311++G(d,p) level. Both ground and excited state geometries were fully optimized in gas phase and in solution. Solution calculations were carried out with Polarizable Continuum Model (PCM). Current results indicate that solvent polarity did not affect Py and its derivatives except PyNH$_2$. Solvent has minor effects on PyCN and PyOH. Although PyNH$_2$ has he smallest HOMO-LUMO energy gap, it is not the best candidate due to its shortest fluorescence lifetime. On the other hand, PyOH and PyCN have longer lifetimes. Therefore, it is concluded that investigated molecules are appropriate candidates for photosensitive applications in the order of PyNH$_2$<PyOH < PyCN < Py.

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1. Introduction

Molecules with conjugated π electronic systems are important as they are potential candidates for use in many different fields of science and technology. The most important group among such molecules includes polycyclic aromatic hydrocarbons (PAHs) which have two or more fused aromatic rings. They have the ability to possess intra- and intermolecular photoinduced charge transfer as a result of π-π interactions. Because of this property, they are preferred in photosensitive material design [1,2].

Pyrene, an optically active polycyclic aromatic hydrocarbon (PAH), has attracted increasing attention because of its intra- and intermolecular photoinduced charge transfer applications [3—9] and its high absorption coefficient, long fluorescence lifetime and high fluorescence quantum yield [10—13]. It is widely used in different optical applications [14—16]. Therefore, investigation of structural, optical and charge transfer properties of pyrene and its derivatives are important. For example, 1-hydroxypyrene (PyOH) (Fig. 1), is a member of molecules classified as photoacids and is widely used to investigate excited state proton transfer systems [17—20].

Pyrene and its derivatives may also display strong bonded and nonbonded interactions with many different types of molecules. Many studies were reported for the development of organic and inorganic photosensitive materials and sensors by using the interactions of Pyrene with CNTs, porphyrins (π-π stacking interactions), phthalocyanines, liposomes, proteins and nucleic acids [21—32]. Additionally, Pyrene-based blue emitters for OLED devices were developed [33—35] and synthesis studies are still in progress for more efficient blue fluorescence emitters in Pyrene electroluminescence [36—38].

Our group also focused on intermolecular photoinduced charge transfer complexes formed by pyrene derivatives and biologically important molecules (aromatic amino acids, some drug molecules etc.) [39—41]. Formerly, intramolecular charge transfer processes for mimicking natural photosynthesis has been investigated in which pyrene acted as a light harvesting antenna [4—6].

In a recent computational work, we have investigated substituent effects on pyrene and its derivatives in different solvents in ground state [42]. However, molecular geometries may change in excited state and using ground state geometries may be insufficient. Additionally, the influence of substituents upon the behaviour of excited states is also still less known of pyrene derivatives.
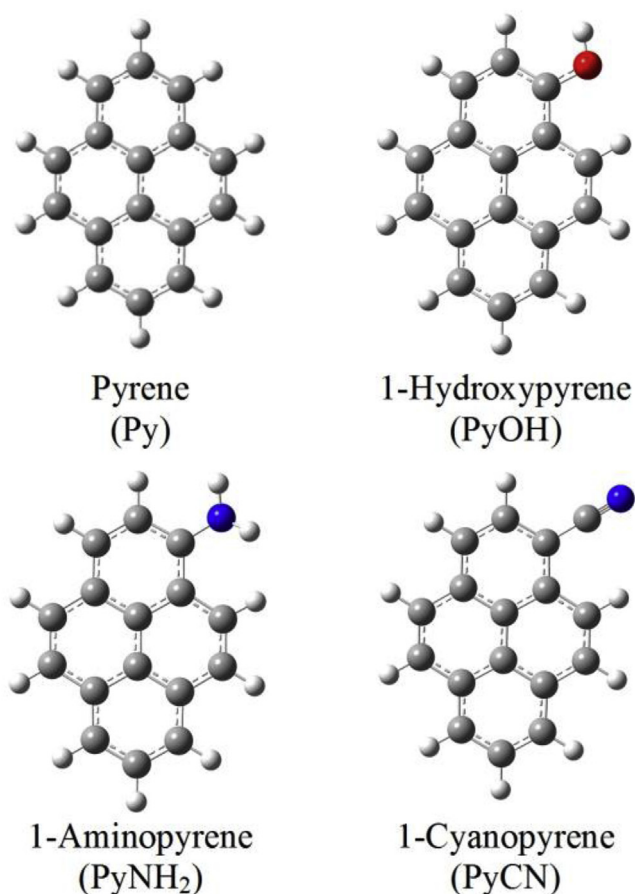
Fig. 1. Molecular structures of Pyrene (Py), 1-Hydroxypyrene (PyOH), 1-Aminopyrene (PyNH$_2$) and 1-Cyanopyrene (PyCN).

Therefore, excited state geometries of pyrene and its derivatives were optimized using Density Functional Theory for a better interpretation of the changes in the spectra. Additionally, ground state geometries from previous study were further optimized at a higher level. UV−Vis absorption, steady-state and time-resolved fluorescence measurements were performed experimentally to compare with computed results.

This study reports spectroscopic and computational investigation of pyrene and its selected derivatives in ground and excited states in solvents with different polarities. Experimental and computational results were compared. Amino and Hydroxy substituents display electron donating character, and cyano substituent has electron accepting character.

2. Experimental and computational details

The properties of the molecules are as follows: Pyrene, Py, (99%, Sigma), 1-Hydroxypyrene, PyOH, (98%, Aldrich), 1-Aminopyrene, PyNH$_2$, (97%, Aldrich), and 1-cyanopyrene, PyCN, (synthesized in a former study [43] with the method given by Tintel et al. [44]). The solvents used are methylcyclohexane (99%, Aldrich, spectroscopic grade), tetrahydrofuran (99.9%, Merck), and acetonitrile (99.8%, Merck).

Perkin Elmer Lambda 35 UV−vis Spectrophotometer was used to record UV−vis spectra. A quartz cuvette with a thickness of 1 cm was used. Perkin Elmer LS-55 Spectrofluorophotometer was used for steady-state measurements. Nitrogen gas was applied during fluorescence and lifetime measurements to minimize the

quenching effect of the dissolved oxygen.

Time resolved fluorescence lifetime values were calculated according to the time-correlated single-photon counting (TCSPC) luminescence by using a SPEX Fluorolog-3 (Horiba-Jobin Yvon) spectrometer attached to an integrated TCSPC software. 295 nm Laserdiode was used as the excitation wavelength source for the lifetime measurements (295 nm nanoled, TAC (time-to-amplitude converter) range: 2 μs, repitation rate: 500 KHz). The temporal evolution of the fluorescence decay was monitored with a microchannel plate (Hamamatsu, R3809U-58) which provides a time resolution of up to 30 ps Emission maximum values of studied compounds were used for measuring fluorescence lifetimes: Py, PyOH, PyNH$_2$ and PyCN (392 nm, 400 nm, 406 nm, and 402 nm in MCH, 392 nm, 400 nm, 426 nm, and 406 nm in ACN respectively) at room temperature. All molecules presented a monoexponential decay curves and fitted with formula A + Bexp(t/τ) using DAS6 program by HORIBA. B is the preexponential factor, A is the offset for the fitting, χ^2 (chi^2) is the quality of fitting and τ is the calculated lifetime in sec.

Initial structures for the investigated molecules were prepared using Spartan 08 [45]. Computational investigation was carried out with Gaussian09 [46], and Gaussview5.0 [47] programs. All ground and excited state geometries of the molecules were optimized by density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods at B3LYP/6-311++G(d,p) level both in gas phase and in solution. Frequency analysis was performed to check the optimized geometries.

TDDFT at the above mentioned level was used to investigate the electronic transitions. 40 first singlet excited states were calculated and used to obtain the spectra for each molecule. Gaussview was used to visualize molecular orbitals and the UV−Vis measurements of the investigated molecules. The total electron density surface of investigated molecules were calculated based on the electrostatic potential values in the gas state and in solution for the excited state optimized geometry.

Solvation effect was taken into account by using the Polarizable Continuum Model (PCM) [48,49] and calculations were carried out in cyclohexane (CH, nonpolar), tetrahydrofuran (THF, medium polar), acetonitrile and water (ACN, and H$_2$O, polar solvents).

3. Results and discussion

3.1. Experimental part: UV−Vis absorption, fluorescence and lifetime measurements

Ground and excited state properties of pyrene (Py), 1-hydroxypyrene (PyOH), 1-aminopyrene (PyNH$_2$), and 1-cyanopyrene (PyCN) were investigated by spectroscopic and computational methods. UV−Vis absorption and fluorescence spectra of studied molecules were recorded in solvents with different polarities. Experimental and computational results for 0-0 transitions were displayed on the same graph. Lifetime measurements were given for the solvents MCH and ACN. Molecular structures of investigated molecules are shown in Fig. 1.

The UV−Vis absorption spectra of investigated molecules in different solvents are displayed in Fig. 2. During the measurements, the concentrations of pyrene, hydroxypyrene, aminopyrene and cyanopyrene were used as 1.2 × 10^{-5} M, 1.5 × 10^{-5} M, 1.17 × 10^{-5} M, and 1.14 × 10^{-5} M respectively to prevent dimer formation. For Pyrene, the 0-0 transition was observed as a very small peak around 371 nm and was accompanied by other very weak vibronic peaks; on the other hand, the strong 0-0 peak corresponding to the second excited state was observed around 334 nm. It was clear that the 0-0 peak became more significant and the vibrational structure shifts by the addition of substituent