



# Fullerene-Benzene purple and yellow clusters: Theoretical and experimental studies



Megan P. Lundgren, Sakiba Khan, Aysegul K. Baytak, Arshad Khan\*

Chemistry Department, The Pennsylvania State University, DuBois, Pennsylvania, 15801, United States

## ARTICLE INFO

### Article history:

Received 22 February 2016

Received in revised form

29 May 2016

Accepted 1 June 2016

Available online 3 June 2016

### Keywords:

Fullerene benzene clusters

Yellow and purple complexes

Experimental spectra

Theoretical spectra

Bucky-Ball benzene cluster

Vertical and parallel clusters

## ABSTRACT

Fullerene (FR, C<sub>60</sub>) gives a purple colored solution almost instantly when benzene is added to it. Interestingly, this purple solution turns yellow in about 7 weeks and remains yellow afterwards. The concentration of the purple complex increases with temperature indicating its formation kinetically favored, which transforms into a more stable yellow complex very slowly with time. The geometry optimization by density functional theory (DFT) followed by spectra (TD-DFT method) calculations suggest that the purple and yellow complexes are due to clusters of six benzene molecules arranged vertically and horizontally respectively around the FR molecule.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Fullerene (FR, C<sub>60</sub>) and its derivatives have been extensively studied for their medical and industrial applications (refs. [1–5], and references therein). The medicinal applications take into account the interaction of drug molecules and drug resistant bacteria with the FR molecule. In nanotechnology and molecular electronics the FR derivatives with different molecules are being examined for their thermal and electrical conductivities. Since the FR molecules and their derivatives have interesting properties with potential applications in wide range of areas, there is a general interest in the study of the interaction of FR and its derivatives with other molecules.

The formation of bright magenta/purple colored solution of FR in benzene (B) has been known to scientists since 1992 when Kroto and collaborators [6] tried to obtain a solid form of the FR compound from its benzene solution. Although they could not obtain a solid purple colored compound, their efforts resulted in a black compound. The X-ray diffraction study characterizes the black compound to be a FR-B<sub>4</sub> cluster. Ying et al. [7] performed light scattering experiments on FR-Benzene solution and noticed that the scattered intensity increases with time and interpreted their

result by assuming the formation of FR clusters in the solution.

In this paper we report formation of a purple complex of FR in benzene solution that in 7 weeks converts into a yellow complex, and then, remains yellow without any further change. Although innumerable studies have already been reported on FR and its derivatives with different organic molecules (refs. [8–12], and references therein), to the best of our knowledge, no studies have so far been reported on the FR-B purple or yellow complex. The earlier studies involved FR complexes with different number (1–6) of substituted tetrazines [8], butadiene [9], methylene [10], pyrrolidine [11] and anthracenes [12]. The computational studies were carried out by applying the DFT method at the B3LYP/6-31G\* level. The present study, done at a higher level of theory, aims at determining the composition and structure of the purple and yellow complexes of FR with benzene molecules by applying both the experimental and theoretical methods.

## 2. Experimental

### 2.1. Preparation of solutions and absorbance measurements

The FR solution (0.40 mg/mL) was made by dissolving solid (Alfa-Aesar, 99.5% purity) in benzene (GFS Chemicals, 99.9% purity). The purple colored solution was then allowed to age in a circulating water bath at 25 °C for over 3 months, and absorbance readings

\* Corresponding author.

E-mail address: [kub@psu.edu](mailto:kub@psu.edu) (A. Khan).

were taken periodically to see how the spectra change with time. Fig. 1 shows the spectrum of the freshly made purple solution from 300 to 700 nm wavelength range, and shows absorbance peaks at around 320 (strong) and 420 nm and smaller peaks between 450 and 650 nm. Fig. 2 shows the enlarged spectra within the wavelength range of 450–650 nm. The temperature effect on the FR-purple complex has also been studied by increasing the temperature of the solution from 15 to 35 °C. A Genesys 2 spectrophotometer was used to take the spectra of these solutions.

## 2.2. Aging time and temperature effect on FR-benzene purple complex

The three upper most curves of Fig. 2 represent spectra of the purple solution at 15, 25 and 35 °C and are represented by filled triangles, circles and squares respectively. These spectra show absorbance peaks at 540 and 600 nm respectively. The dashed line shows the tail section of the 540 nm peak, and allows us to resolve the 25 °C spectrum to component peaks at around 540 and 600 nm (smallest peak with open circles) with intensity ratios of around 2.5 and 1. Hence, Figs. 1 and 2 show the experimental peaks at 320, 420, 540 and 600 nm with relative intensities of 27, 2, 1 and 0.4 respectively. Although the color of the purple solution remained purple even after heating, it changed to yellow after 7 weeks of aging at 25 °C. The bottom curve with a thick solid line represents the spectrum of the yellow solution with significantly diminished peak intensity at 540 nm, increased intensity at 420 nm and almost unchanged intensities at 600 and 320 nm suggesting that the 600 and 320 nm peaks are not associated with the purple or yellow FR-B (FR-benzene) complex. Indeed, the 600 and 320 nm peaks have been observed in gas phase FR [13,14] spectrum suggesting that they are due to isolated FR molecules or FR clusters. These analyses suggest that the absorbance peaks at 420 and 540 nm are associated with the FR-B purple complex, and only the 420 nm peak is associated with the yellow complex. It is interesting to point out that once the yellow complex is formed after 7 weeks of aging in the bath, it remains yellow even after aging for a longer period of time (3 months), or even after heating to a high temperature (boiling), suggesting stability of this yellow complex.

## 3. Computational methods

In order to determine the composition and structure of the

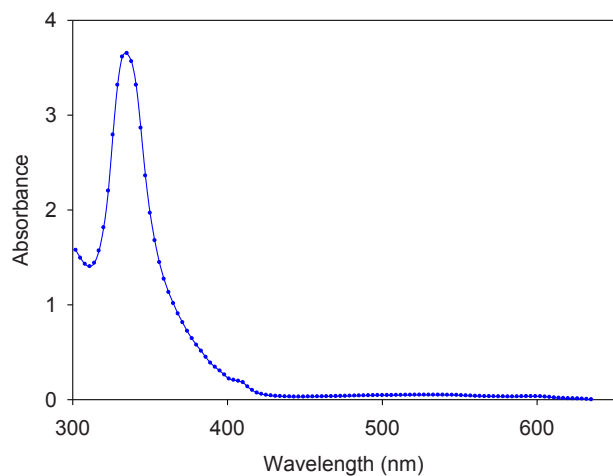


Fig. 1. Spectrum of the purple solution within the wavelength range of 300–650 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

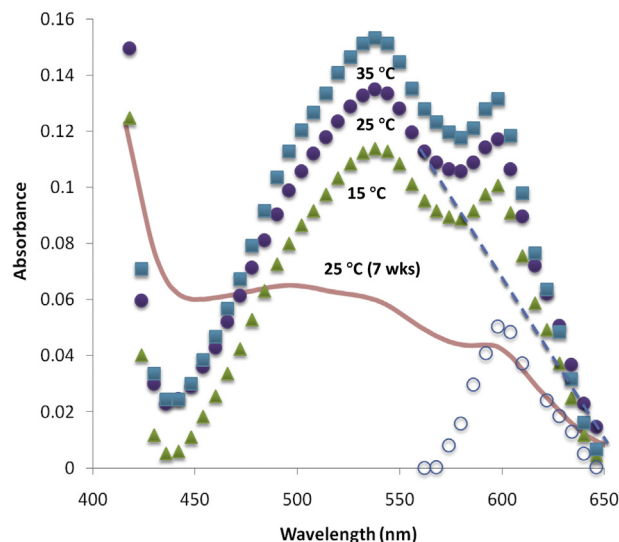


Fig. 2. Spectra of purple Fullerene-benzene (FR-B) solutions at 15, 25 and 35 °C represented by filled triangles, circles and squares within the range of 430–650 nm. The dashed line for 25 °C curve represents the tail section of the 540 nm peak, and has been used to determine the intensity of the component peak at 600 nm, which is shown with open circles. The spectrum of the yellow solution is shown with a thick curve and a highly diminished 540 nm peak. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

purple as well as the yellow FR-B complex, a number of density functional theory (DFT) calculations were carried out by using the Gaussian 09 software package [15]. The FR molecules with varied number (1–8) of benzene (B) molecules around were considered for these studies. Each assumed structure was optimized by applying the B3LYP method [16–19] and using the 6-31G\* and then, 6-31 + G\* (for FR-B<sub>6</sub>) basis sets followed by a single point energy calculation with a larger basis set (6-311 + G\*). Time dependent DFT (TD-B3LYP) calculations of electronic absorption spectra were performed on the optimized structures by using the 6-31G\* basis set. These calculations involved 60 singlet and 60 triplet excited states. The FR-B complexes with varied number of benzene molecules that show at least one spectral peak close to that of the experiment are presented in Table 1. In addition to gas phase calculations, the solvent effect on stabilization energy (SE) has also been examined by applying the polarized continuum model (PCM)

Table 1

Calculated energy (E) values are presented for different Fullerene-Benzene (FR-B) clusters. Energy values were calculated at the B3LYP/6-311 + G\* level after geometry optimization by 6-31 + G\* basis sets. Both vertical and horizontal orientations of the benzene rings around the FR molecule were examined together with the dispersion corrected values (in parenthesis) for FR-B<sub>6</sub>, FR, and B. The calculated spectral peak positions with relative intensities (in bracket) are also presented. The dispersion corrected stabilization energy (SE) values relative to separated constituent molecules (FR, B) are also presented.

Molecule	Energy (H) (at 6-311 + G* basis)	SE (Kcal/mol)	Calc. peaks, nm (Intensity ratios)
FR-B4 (vert)	–3215.171702		545, 438 [1:5]
FR-B4 (hor)	–3215.173264		544, 437 [1:17]
FR-B6 (vert)	–3680.416389 (–3680.582381)	16.7	544, 437 [1:3] expt. 540, 420 [1:2]
FR-B6 (hor)	–3680.418452 (–3680.589039)	20.9	436 (only peak) (expt 420, only pk)
FR-B8 (vert)	(–4144.169199)		548; 437 [1:20]
FR	–2286.609611 (–2286.721531)		
B	–232.300650 (–232.305705)		

Download English Version:

<https://daneshyari.com/en/article/1404716>

Download Persian Version:

<https://daneshyari.com/article/1404716>

[Daneshyari.com](https://daneshyari.com)