Research Article

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The Study of the Optical Properties of C₆₀ Fullerene in Different Organic Solvents

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Abstract: C₆₀ fullerene exhibits unique optical properties that have high potential for wide photo-optical applications. To analyze the optical properties of C₆₀, its excitation and emission properties were studied using UV-Vis absorption and photoluminescence (PL) spectroscopy, which were performed in various, non-polar organic solvents such as toluene, xylene, and trichloroethylene (TCE). The C₆₀ solutions in toluene, xylene, and TCE displayed similar excitation bands at 625, 591, 570, 535, and 404 nm corresponding to $A_g \rightarrow T_{1u}$ and $A_g \rightarrow T_{1g}$ transitions. However, these bands differed from the solid C₆₀ observed by UV-Vis diffuse reflectance spectroscopy. The two emission band energies of C₆₀ solution in toluene and xylene were nearly the same (1.78 and 1.69 eV), whereas the C₆₀ solution in TCE was shifted to 1.72 and 1.65 eV. Because the polarity of TCE is higher than that of toluene and xylene, the PL spectrum of the C₆₀ solution in TCE was red-shifted. The PL spectroscopy had a better capability than UV-Vis absorbance spectroscopy to distinguish the different interactions between C₆₀ and the organic solvents due to their different solvent polarities.

Keywords: C₆₀; UV-Vis absorption; photoluminescence; solvatochromism; solvent polarity.

1 Introduction

The allotropes of carbon nanostructure material—such as graphite, graphene, diamond, fullerenes, carbon nanotubes, amorphous carbon, and carbyne—have received great interest due to their chemical and physical properties. Each allotrope exhibits different properties depending on its carbon structure and size. According to carbon hybridization, graphite and graphene have sp²-hybridized carbon atoms, while a diamond has sp³-hybridized carbon atoms. Amorphous carbon mostly consists of sp²-hybridized carbon atoms, and carbyne has sp-hybridized carbon atoms. The other carbon allotrope materials—fullerenes and carbon nanotubes—have quasi-sp² hybridization [1].

Fullerene takes the spherical shape of graphene and was discovered through the laser evaporation of graphite by Kroto in 1985 [2], who won a Nobel Prize in 1996 for this discovery. Unlike graphite or graphene, which are predicted to be in planar geometry in their stable form, spherical fullerene has a pyramidalization angle ($\theta_{\text{pyr}} - 90^\circ$) depending on the number of carbon atoms. This pyramidalization angle can force carbon atoms to have a spherical geometry. One example of the pyramidalization angle belonging to C₆₀ fullerene is 11.6° [3, 4], which means that a 101.6° angle was formed between the σ and π orbitals in a carbon atom. Among various types of fullerene, the most commonly known and most stable species is Buckminsterfullerene, or C₆₀ [5–7]. C₆₀ fullerene is soluble in non-polar or slightly polar organic solvents. The non-polar solvents, such as toluene, o-xylene, carbon disulfide (CS₂), dichlorobenzene (DCB), etc., are commonly used to extract the fullerenes from freshly prepared carbon soot after the synthesis process.

The growing interest in C₆₀ has encouraged more studies in various fields, the number of which has continued to grow since the discovery of C₆₀ fullerene, and C₆₀ has been applied in various applications due to its unique chemical and physical properties. These applications include supercapacitors [8, 9], hydrogen

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storage [10, 11], nanoelectronics [12, 13], and biomedical applications such as gene and drug delivery [14, 15]. Additionally, the quasi-sp²-hybridized carbon belonging to C₆₀ supports the high electronic conductivity in charge transportation and separation [16]. Therefore, C₆₀ and its derivatives have many potential uses in optics due to their electron-accepting characteristics and photophysical properties.

C₆₀ exhibits several unique electronic properties related to its optical characteristics and photoluminescence (PL). PL is a process in which a molecule spontaneously emits light after absorbing a photon, which enables the electrons to be excited to a higher electronic state. The emitted light is a result of the electron returning to its lower energy state, which is known as fluorescence and phosphorescence [17]. In general, the illustration of the excitation-emission mechanism is commonly understood using the Perrin-Jablonski diagram [18]. Carbon nanomaterial exhibits different PL characteristics depending on its architecture, size, morphology, and structure. For example, diamond and bulk graphite do not exhibit PL due to their infinite carbon networks. However, a spherical fullerene is able to produce strongly environment-dependent PL, which is emitted from the lowest energy singlet-electronic excited state to the ground state in the Vis-NIR region [19].

Theoretically, the PL process is influenced by the environment, the solvent, and the temperature. In general, at low temperature, the PL of fullerene is weak. Similarly, if the fullerene solubility is low in solvent, then the PL will also be weak. Furthermore, because fullerenes are good electrophiles, they can form both ground and excited-state complexes with many aromatic solvents, resulting in strong solvatochromism [19]. In the solvatochromism phenomenon, the intermolecular interactions affect the excitation and emission properties induced by the solute-solvent interaction [20].

The optical properties of fullerene have been widely investigated in different solvents by spectroscopy, and the published studies on the comparisons of C₆₀ optical properties have agreed on solvents with significant different polarity, including toluene [21-24], o-xylene, dichlorobenzene (DCB) [25], hexane [22, 26], cyclohexane [27], methylcyclohexane, CS₂ [28], acetonitrile [23], alkanes [29], and water [30-32]. However, the interpretation of the findings has revealed unpredictable results due to the unknown dynamic phenomenon caused by inter and intra-molecular interactions. Since the chemical structures and polarity of the solvents influence the optical properties of the C₆₀ solution [33-35], intermolecular interactions such as Coulomb and dispersion forces and electron-charge transfer forces might be produced by the solute-solvent

interactions. These interactions are defined by the solvent polarity and are expected to have a significant role in the photochemistry of fullerenes. Besides the intermolecular interaction, the other factor that should also be considered is the intra-molecular interaction involving the Jahn-Teller (JT) distortions and Herzberg-Teller (HT) vibronic coupling [18, 20, 28, 29, 36, 37].

Due to its unique optical properties, C₆₀ is used in various applications, including solar cells [38, 39], light to electrical energy converters in photovoltaic devices [40-44], photocatalysts [45-49], phototherapy [50, 51], bioimaging [52, 53], and biosensing [54-56]. C₆₀ possibly exhibits the optical response depending on the changing of the environment; however, the relevant studies on this sensitive response are still limited. Therefore, this study examined the optical properties of C₆₀ fullerene, including the excitation and emission characteristics found in organic non-polar solvents with slightly different polarity.

To study the sensitive optical response of C₆₀, different solvents were selected that had similar chemical structure and polarity; these were toluene and xylene. Moreover, to study the polarity effect, another solvent with a slightly higher polarity compared to toluene and xylene was chosen; this solvent was trichloroethylene (TCE). These three solvents were considered suitable for studying the solvatochromism phenomenon based on the PL spectra revealed by different C₆₀ solutions. Therefore, this study aimed to confirm that the solvents with slightly different chemical structure and polarity would responsively provide different molecular interactions with C₆₀ fullerene by producing spectra with apparent characteristics.

Additionally, this study compared the absorption spectra of solid C₆₀ and its solutions in different solvents to demonstrate the environment-sensitive optical response characteristics. A comparison to pioneering works, both theoretical and experimental, was also performed. The results reported in the present study indicated the potential use of C₆₀ as a controllable fluorescent material in imaging and optoelectronics applications.

2 Methods

The concentration of the C₆₀ fullerene solution was made 0.1 (w/v)% by dissolving 0.003 g C₆₀ (95%; Hengqiu Graphene Technology [Suzhou] Co., Ltd) in 3 mL of each of the following solvents: toluene (Merck, ≥99.9%), xylene (Pudak, isomeric mixture), and TCE (Merck, ≥99.5%). An absorption spectra scan was performed on the C₆₀ solution in these three solvents. The absorbance measurement was carried out using a spectrophotometer (MayaPro2000

Ocean Optics) with a halogen lamp source (300 nm to 1100 nm). The solution was put in a quartz cuvette, and its absorbance was measured at wavelengths from 300 nm to 1100 nm. The chemical information of functional groups and the purity and morphological properties of the solid C_{60} were examined by Fourier transformed infrared (FTIR; IRPrestie-21, Shimadzu), Raman spectrometer (Modular Raman Spectroscopy – iHR550, Horiba), and scanning electron microscopy (SEM; FEI Inspect-S50), respectively. The solid C_{60} was also characterized by using UV-Vis diffuse reflectance spectroscopy (Pharmaspec UV1700, Shimadzu), in which the data was further compared to the optical data of C_{60} in solvents.

The PL properties of the C_{60} solutions in different solvents were investigated using a home-made PL spectrophotometer consisted of a spectrograph (MayaPro2000 Ocean Optics), a laser diode (420 nm, 5 mW), and the plano-convex lenses. The radiated laser was caught by the first lens and focused on the cuvette of the sample. The laser hit the clear front side of the cuvette at a 45° angle. This light beam of the emission was then reflected onto the second lens. The second lens gathered the light scattered from the cuvette, and this light was then refocused by the third lens, allowing the light to be caught by the spectrometer via a fiber optic and then analyzed by a computer. To learn the band energies observed in the absorption and PL spectra, equation (1) was applied.

$$E = h \frac{c}{\lambda} \quad (1)$$

where E is energy, h is Planck's constant (6.63×10^{-34} J s), c is the speed of light, and λ is wavelength.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and Discussion

The C_{60} geometric structure has Ih symmetry in the solid phase, as seen in Figure 1(a). If a possible reaction causes C_{60} symmetry to change, the C_{60} optical properties can also change. The solid C_{60} was firstly characterized by FTIR, Raman spectrometer, and SEM to test the original characteristics compared to relevant references. The FTIR and Raman spectra of the solid C_{60} are presented in Figure 1(b) and (c), respectively. The C_{60} was expected to have only four infrared active vibrational modes (of species T_{1u}) occurring at about 1600 ± 200 , 1300 ± 200 , 630 ± 100 , and 500 ± 50 cm^{-1} [57].

As shown in Figure 1(b), the spectrum of the solid C_{60} revealed several relevant absorption peaks at 526.6,

575.8, 1181.4, and 1428.3 cm^{-1} (attributed to C–C vibrational modes) and 3460 cm^{-1} (attributed to O–H stretching). All these peaks were found in agreement with previous studies [30, 57–59]. The O–H stretching peak had broad shape with less intensity, which strongly suggested that it came from air adsorbed in the material's pores rather than as a hydroxyl functional group attached to carbon. This suggestion was supported by the fact that no broad peak C–OH observed at 1107 cm^{-1} was found [30]. The observation of these peaks showed that the C_{60} sample used in this study was original C_{60} with high purity.

Raman spectrometry was also a useful technique for the characterization of disorder in carbon-based materials. The analysis of specific features in the Raman spectra provided a way to estimate the crystallite sizes in disordered carbons [60]. Therefore, to confirm that the C_{60} sample in a solid state had good and stable properties, the Raman spectrum of sample was characterized, as shown in Figure 1(c). The vibrational modes of the solid C_{60} were divided into intermolecular vibrations (or lattice modes) and intra-molecular vibrations (simply molecular modes), and the first mode lay at lower frequencies, while the latter one lay at a higher frequency (above 270 to 1700 cm^{-1}). The higher frequency was observed to be more dominant. The characteristics of the Raman spectra were in accordance with the literature [61, 62], which previously reported several peaks at a Raman shift of 272, 432, 496, 709, 772, 1099, 1249, 1422, 1467, and 1573 cm^{-1} . Additionally, the Raman active modes had $2A_g$ and $8H_g$ symmetry. The C_{60} spectrum had two relatively sharp lines at around 496 and 1467 cm^{-1} , known as the breathing mode, $A_g(1)$, and pentagonal pinch mode, $A_g(2)$, respectively [61, 62]. 1A_g is the ground state of C_{60} issued from the closed shell electron configuration of $a_g^2 t_{1u}^6 h_g^{10} t_{2u}^6 g_u^8 g_u^8 h_g^{10} h_u^{10}$ [26]. The other peaks at 272, 432, 709, 772, 1099, 1249, 1422, and 1573 cm^{-1} corresponded to $H_g(1)$ to $H_g(8)$ modes [61, 62]. The sharpness of the bands indicated that the bonds were mostly uniform in nature.

According to the SEM analysis, as shown in Figure 1(d) to (e), the solid C_{60} consisted of particulate aggregated C_{60} ~200 nm with a regular spherical form. Smaller-sized particle grains were also observed, as indicated by the red rectangle in Figure 1(d) and emphasized in Figure 1(e).

Many researchers have studied the optical properties involving the fluorescence of C_{60} as revealed in different solvents. This study, however, used three kinds of organic solvents—toluene, xylene, and TCE. In this experiment, the color of the C_{60} solution in both the toluene and xylene solvents turned purple, and it was a darker purple in the TCE, as seen in Figure 2. The same purple color was seen in the toluene and xylene solvents possibly due to the similar

Figure 1: (a) The I_h symmetry structure of C_{60} , (b) FTIR, (c) Raman spectrum of solid C_{60} , and (d-e) the SEM imaging of solid C_{60} at a different magnification.

Figure 2: The C_{60} solution in different organic solvents: (a) toluene, (b) xylene, and (c) TCE.

structure of these two solvents consisting of a benzene ring and methyl group. In contrast, TCE has a different structure consisting of a halogenated hydrocarbon compound with no benzene ring.

As mentioned in the introduction, due to fullerene structure consists of an sp^2 -hybridized carbon atom, C_{60} is mostly dissolved in a non-polar organic solvent with different solubility [63]. The solubility of fullerene is determined by a geometric factor and the specific molecular interactions between fullerene and the solvent molecules. The interactions are influenced by several solvent properties, such as polarizability, polarity,

molecular size, and cohesive energy density [63]. The polarizability is defined by the ease of electron cloud distortion that causes the originally non-polar molecule or atom to acquire a dipole moment. The polarity indicates the distribution of the electrical charge over the molecules and is closely related to the relative electronegativities of the elements. Applying the “like-dissolves-like” concept, the identical polarizability and polarity for solute and solvents achieves better interaction between them, thus increasing solubility. For instance, as Ruoff et al. [63] reported, the non-polar sp^2 carbon atom characteristics of C_{60} have better solubility in xylene (5.2 mg/L) than in toluene (2.8 mg/L). The solubility of C_{60} in TCE was found to be less than the solubility in both toluene and xylene, at 1.4 mg/L. The solubility of C_{60} in alkanes such as n-pentane, n-hexane, etc. was very low (~ 0.005 to 0.04 mg/L), far from the solubility in toluene and xylene [63].

The illustrations of the interaction between C_{60} and the solvents are presented in Figure 3. The three solvents—toluene, xylene, and TCE—had distinguished dipole moments of 0.31 D, 0.45 D, 0.31 D, 0 D, and 0.81 D, for toluene, o-xylene, m-xylene, p-xylene, and TCE, respectively [64]. These moments might have corresponded to their dielectric constants [63, 65]. For comparison purposes, C_{60} had a dipole moment of 0.47 D [63]. In the interaction between C_{60} and toluene or xylene, due to

the similar chemical structure consisting of a hexagonal ring of carbon, C_{60} acted as a π -acceptor, as illustrated in Figure 3(a) to (b). Therefore, the interaction between C_{60} and toluene/xylene occurred as a weaker intermolecular interaction—the Van der Waals interaction—which accounted for the London dispersion forces, particularly the $\pi - \pi$ interactions between the hexagonal ring of carbon as shown in Figure 3(a) and (b).

In contrast, due to the slightly polar chemical structure of TCE (as compared to toluene/xylene, even though all the solvents were non-polar and organic), the interaction between C_{60} and TCE, as shown in Figure 3(c), occurred as dipole-induced dipole intermolecular interaction, which is defined as the interaction between the permanent dipole belonging to TCE and the induced dipole of the C_{60} . Moreover, C_{60} acted as an effective electron acceptor, while TCE acted as the potent donor electron. The TCE molecules were adducted to C_{60} through charge transfer, similar to the interaction between fullerene and dimethyl sulfoxide (DMSO) reported by Zhang et al. [66]. However, regarding the “like-dissolve-like” concept, because TCE and C_{60} had dissimilar chemical structures, the C_{60} solubility in TCE was lower than in the other two solvents, which induced a weaker interaction.

Therefore, because the solute-solvent interactions might be different, the solvent induces different optical characteristics of the C_{60} solutions. The solvent interacts with the solute in its ground state or excited state through intermolecular bonding. In general, a polar solvent like water is capable of hydrogen bonding with the solute if the solute has a hydrogen-bonding component or if there are induced dipole-dipole interactions. In contrast, non-polar solvents can interact through polarizability via London interactions.

The UV-Vis absorption spectra of C_{60} in the different solvents (toluene, xylene, and TCE) are shown in Figure 4(a). The C_{60} solutions in the toluene, xylene, and TCE solvents revealed an absorbance around 404, 535, 570, 591, and 625 nm, as shown with arrows in Figure 4. These bands corresponded to the electronic transitions of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$. This result was nearly the same as that produced by Zhang et al. [23] and Törpe and Belton [25], who found that the main absorption bands of C_{60} in toluene and o-xylene occurred at a wavelength of ~ 407 nm in a sharp feature attributed to the lowest energy ${}^1T_{1u}$ state [67], followed by a broad absorption band in the range of 430 to 650 nm [23, 25]. This broad band was attributed to multiple vibronic excitations activated through an HT coupling orbital to the JT distorted orbital at a higher level, assigned as forbidden singlet-singlet transitions [26]. This experimental absorption feature was in agreement with

Figure 3: Illustration of the presumptive interaction of C_{60} with three solvents: (a) toluene, (b) xylene, and (c) TCE.

the pioneering works that reported the absorption spectra of C_{60} in toluene [68, 69], o-xylene [25], n-hexane [26, 70–72], and N-methyl-pyrrolidine (NMP) [73].

However, the absorption spectra of C_{60} in toluene or xylene exhibited a comparatively positive solvatochromism (bathochromic [red] shift) of the weak $n \rightarrow \pi^*$ absorption bands. As shown in Figure 4(b), compared to the absorption peaks observed in the spectra of C_{60} in toluene and xylene, those observed in the spectra of C_{60} in TCE slightly shifted to the lower wavelength. However, the intense $\pi \rightarrow \pi^*$ transition band in the ultraviolet region was less sensitive to the solvent changes [74], which possibly indicated that there was no significant symmetry degradation of C_{60} , even though the interaction between C_{60} and the solvent was possibly different.

To study the interactions of C_{60} with a different solvent, the results shown in Figure 4 were compared with the absorption and reflectance spectra of the solid C_{60} , as shown in Figure 5. The absorbance and reflectance spectra taken by a diffuse reflectance spectrometer are presented in Figure 5(a) to 5(d), which is a plot of log absorbance and reflectance (%) versus wavelength ranges from 200 to 800 nm. Figure 5(a) shows the absorption spectrum of the solid C_{60} . The dashed rectangle in Figure 5(a) is emphasized in Figure 5(c). The emphasized absorption area of the solid C_{60} shown in Figure 5(c) was presented together with the absorption spectra of the C_{60} solution in three different solvents for comparison. The absorption spectrum of the

solid C₆₀ was different than the C₆₀ in solvents. All spectra presented had similar absorption bands at around 404, 590, and 625 nm. However, the absorption bands located at 535 and 570 nm were only found in the absorption spectra of the C₆₀ solutions. The absorption peak at 404, 590, and 625 nm in the C₆₀ solution was red-shifted to 414, 597, and

675 nm in the solid C₆₀, as listed in Table 1, indicating the presence of stronger absorption across the gap between the highest occupied molecular orbital and lowest unoccupied molecular orbital (HOMO-LUMO) in the C₆₀ solution [75].

Figure 5(b) shows the reflectance spectrum of C₆₀. The dashed rectangle in Figure 5(b) is emphasized in Figure 5(d). The arrows shown in Figure 5(a) and 5(b) represent the region where the absorption declined, which was later used to estimate the band gap energies using the Kubelka-Munk function [76, 77] as shown in equations (2) and (3), as follows:

$$F(R) = \frac{(1 - R^2)}{2R} \quad (2)$$

$$\alpha \cdot h \cdot \nu = B(h \cdot \nu - E_g)^n \quad (3)$$

where R is reflectance. $F(R)$ is proportional to the extinction coefficient (α). The Kubelka-Munk function modification can be applied by multiplying the function $F(R)$ by $h \cdot \nu$, using the coefficient (n) associated with the electronic transition based on equation (3). B is the absorption constant, and $n = 1/2$, plotted as $(\alpha \cdot h \cdot \nu)^2$ versus E for the direct allowed transition because, according to the band diagram structure, C₆₀ had direct transition [78]. The plotting of α versus E and $(\alpha \cdot h \cdot \nu)^2$ versus E is shown in Figure 6(a) to (b), respectively. The optical gap

Figure 4: The absorbance of C₆₀ solution in different solvents: (a) full spectra and (b) emphasized spectra. The arrows show the absorption peaks, whereas the thin blue and red lines in (b) indicate the shifting of the represented peak.

Figure 5: (a) The absorbance and (b) reflectance spectra of the solid C₆₀; (c) and (d) are the emphasized region of the dashed rectangular regions in (a) and (b), respectively, compared to the absorption in C₆₀ solutions in different solvents.

Figure 6: The Kubelka-Munk function of the solid C_{60} (a-b) and the extrapolation of onset peak in four regions emphasized in (c) to (f).

energies were then determined by an intersection of the linear extrapolation at the falling peak edge of the onset of the spectra, as shown in Figure 6(c) to (f), indicated by numbers 1 to 4.

The band energies estimated from four regions (1 to 4) were 4.75, 3.68, 2.75, 1.92, and 1.69 eV and are represented in Figure 6(c) to (f), respectively. Theoretically, the C_{60} crystal had a narrow-band semiconductor with the energy gap between the HOMO-LUMO of 1.5 to 2.6 eV, which is optically forbidden. The experimental evidence showed different values of the energy gap, ranging also from 1.69 to 4.82 eV (listed in Table 1). These results were also in agreement with the results published by Ren et al. [75] who reported three band energies of C_{60} film at 4.72, 3.65, and 2.75 eV.

According to the electronic structure of the C_{60} molecule, these band energies were the symmetry-allowed transitions that may be assigned as $H_u \rightarrow H_g$ (~4.6 eV), $H_g \rightarrow T_{1g}$ (~3.6 eV), and $H_g \rightarrow T_{1u}$ (~2.8 eV) [79]. Zhou et al. reported that solid C_{60} had an E_{gap} ranging from 1.63 to 1.75 eV, which was determined from the Tauc plot calculated from the spectra taken from photothermal deflection spectroscopy [79]. Compared to the solid C_{60} , the C_{60} solution had a lower wavelength (i.e., higher energy gap). This phenomenon was induced by changing the strength of the intermolecular interaction between the C_{60} molecules that were interfered by the solvents, which resulted in the UV-Vis absorption spectra differences. The comparison of wavelength and of the energy gap in this discussion is listed in Table 1.

Table 1: The comparison of the observable absorption band (in nm) and energy gap (in eV) of the C₆₀ solutions, the solid C₆₀, and the Hückel calculation.

Absorption electronic transitions	Excitation bands of C ₆₀ in different phases							
	solution ^a		solid ^b		solid ^c		C ₆₀ molecules ^d	
	nm	eV	nm	eV	nm	eV	nm	eV
* (1): $H_u \rightarrow T_{1u}$	625	1.99	675	1.84	735	1.69	654	1.897
	591	2.10			647	1.92		
	570	2.18			-	-		
(2): $H_u \rightarrow T_{1g}$	535	2.32	597	2.08	-	-	495	2.506
(3): $H_u \rightarrow H_g$	-	-	-	-	261	4.75	258	4.816
*(4): $H_g \rightarrow T_{1u}$	404	3.07	414	3.00	451	2.75	435	2.857
(5): $H_g \rightarrow T_{1g}$	-	-	-	-	337	3.68	358	3.466

Note: For ^a, ^b, and ^c, the data were taken from Figures 4 to 6, respectively; For ^d, the data were estimated using the Hückel calculation [80, 81]; (1) to (5) corresponds to the red upward arrows in Figure 7. *JT and HT effects possibly occurred.

Figure 7: Schematic of the electronic structure of C₆₀ as calculated by the Hückel model [80, 81] and its possible electronic excitation transitions experimentally observed in this study. The electronic excitation and emission transitions were numbered in the bracket as (1) to (5) and (6) to (7), respectively.

The schematic electronic transitions and their summaries are presented in Figure 7 and Table 1, respectively. The possible HOMO-LUMO gap of the solid C₆₀ was obtained at 1.69 eV. This value was 10% to 15% smaller than the band gap energy of the C₆₀ solution, which was 1.99 eV (this was also in agreement with previous results) [81]. Experimentally, five possible excitation transitions existed, as illustrated in Figure 7 by

arrows (1) to (5) (i.e., $H_u \rightarrow T_{1u}$, $H_u \rightarrow T_{1g}$, $H_u \rightarrow H_g$, $H_g \rightarrow T_{1u}$, and $H_g \rightarrow T_{1g}$, respectively). The excitation transition of $H_u \rightarrow T_{1u}$ and $H_g \rightarrow T_{1u}$ might have corresponded to different energies because of the HT and JT active modes. HT modes induced vibronic transition at H_u and H_g orbitals, and the JT distortion effect possibly occurred to the T_{1u} orbital [26, 82, 83].

Figure 8: The PL spectra of C_{60} in the different solvents of (a) toluene, (b) xylene, and (c) TCE; (d) the compilation of PL spectra after being subtracted and (e-f) their emphasized regions.

Following the study of the absorption spectra, the PL spectra were then measured. The PL spectra of the solvents and the dissolved C_{60} in each of the solvents are shown as red and blue dashed lines, respectively, in Figure 8(a) to (c). As seen in the generated spectra, the PL intensity of C_{60} in xylene was higher than in other solvents, which might have corresponded to its higher solubility, as discussed earlier. The PL band characteristic of C_{60} in xylene was similar to that of C_{60} in toluene. Meanwhile, the emission generated by the C_{60} dissolved in TCE was far less intense than that of the other solvents.

The PL spectra of the C_{60} solution consisted of the PL of interacted C_{60} and the solvents used in each C_{60} solution, as shown in Figure 8. The solvent used may have interfered with the original PL of C_{60} . Each of the solvents had their own characteristic PL, as shown in Figure 8(a) to (c) in

blue dashed lines that represent toluene, xylene, and TCE, respectively. For example, in the 600 to 900 nm region, toluene had a PL that coincided with the subtracted PL of C_{60} , but at different intensities. On the other hand, xylene and TCE had different PL characteristics at 650 to 750 nm and 400 to 700 nm, respectively. Thus, the PL profile of the C_{60} solution could have been superimposed with PL from the solvents. Therefore, to identify the emission profile spectra of the interacted C_{60} , the PL spectra of the dissolved C_{60} were subtracted by the PL spectra of the solvents alone. The results of the subtracted spectra are shown as solid black lines in Figure 8(a) to (c). The comparison and normalization of the C_{60} solution were finally given to the spectra divided by the max intensity, as shown in Figure 8(d) to (f).

Table 2: The emission bands of C₆₀ in different solvents after subtraction.

Emission electronic transitions		PL (emission) bands [#]					
		C ₆₀ in toluene		C ₆₀ in xylene		C ₆₀ in TCE	
		nm	eV	nm	eV	nm	eV
*(6): $H_u \leftarrow T_{1u}$	P5	697.20	1.78	697.20	1.78	-	-
	P5'	-	-	-	-	720.46	1.72
	P6	735.63	1.69	735.63	1.69	-	-
	P6'	-	-	-	-	750.77	1.65
*(7): $H_g \leftarrow T_{1u}$	P1	432.74	2.87	431.82	2.88	438.77 (sh)	2.83 (sh)
	P2	440.62	2.82	439.70	2.82	-	-
	P3	443.87	2.80	443.40	2.80	-	-
	P4	460.98	2.69	460.52	2.70	-	-

Note: [#] The data were taken from Figure 8; (6) to (7) correspond to the purple downward arrows in Figure 7; * JT and HT effects possibly occurred; sh = shoulder.

After being subtracted, the PL spectra of the C₆₀ solution in toluene and xylene revealed emissions on the longer wavelength region than the excitation wavelength (i.e., >420 nm region), as presented in Figure 8(d). As seen in Figure 8(a) to (f), the spectra of C₆₀ in the TCE solvent indicated a difference compared to the other solvents. Unlike the C₆₀ solution in toluene and xylene, the C₆₀ in TCE revealed no emission in the 430 to 470 nm region. This phenomenon might have been relevant to the solubility of C₆₀ in TCE. The solubility of C₆₀ in TCE was lower than in the other two solvents, allowing the resulting spectra to have lower intensity and a different emission wavelength. The toluene and xylene solvents had a similar structure, in which they had a benzene ring attached by one and two methyl groups, respectively. Therefore, because the chemical structure was not significantly different, the interaction between fullerenes and toluene or xylene molecules was similar.

The experimental fluorescence features of C₆₀ in toluene or xylene in the wavelength of 430 to 900 nm, as shown in both of Figure 8(e) to (f), were almost the same with the C₆₀ fluorescence spectra in benzene and toluene reported in pioneering studies. Zhang et al. reported an intense emission peak at 440 nm and a broad peak in the region of 600 to 800 nm [23, 66]. The broad emission in the region of 600 to 800 nm was also reported by Palewska et al. [70] and Zhao et al. [84]. They also confirmed that C₆₀ fluorescence in different solvents, such as benzene, toluene, n-hexane, CS₂, and DMSO, reveals different features [70, 84]. However, the fluorescence of C₆₀ in TCE has not been reported elsewhere.

The PL transitions possessed by the C₆₀ solution after the subtraction are listed in Table 2. The presented PL

band data were obtained from the normalized data of the subtracted spectra of C₆₀ solutions and the solvents in nm and were converted to band energies in eV. P1 to P4 and P5 (P5') to P6 (P6') are identified as $H_g \leftarrow T_{1u}$ and $H_u \leftarrow T_{1u}$ emission transitions, respectively. In these transitions, the HT and JT effect might have caused vibronic transitions, as discussed earlier, thus revealing the different emission band energies.

According to the recorded phenomena, the illustration of the solvent effect on the fluorescence emission of C₆₀ is shown in Figure 9. At first, when C₆₀ was surrounded with the solvent molecules, the dipole moments of the solvent molecules could interact with the dipole moment of C₆₀ to yield an ordered distribution of solvent molecules around C₆₀. In the case of a non-polar solvent with no dipole moment, the fluorophore (C₆₀) was not affected. Therefore, when the solvent molecules surrounded C₆₀, the solvent dipole moments interacted with the dipole moments of C₆₀ to align the solvent dipoles with the C₆₀ dipoles.

As illustrated in Figure 9, after C₆₀ was excited from the ground state (S₀) to the higher vibrational levels of the first excited singlet state (S₁; Step 1), the excited C₆₀ and solvent dipoles became unaligned. At the excited state, the excess vibrational energy was rapidly lost to surrounding solvent molecules as C₆₀ slowly relaxed to the lowest vibrational energy level of the solvent excited state (S₁') namely the vibrational and solvent relaxation with no radiation (Steps 2 to 4). In the latter step, the dipole moments were re-aligned. Furthermore, when C₆₀ lay in the lowest energy level of the solvent excited state, it returned to the ground state of C₆₀. As shown in Figure 9, the more polar solvents produced a narrower emission gap; that is, a bathochromic/red-shift (shifting to longer

Figure 9: The illustration of the solvent effect to fluorescence emission of C_{60} in different solvents: (a) toluene or xylene, and (b) TCE. S_0 , S_1 , and S_1' were notable for the ground state and excited state of C_{60} and the excited state of the solvent. The number indicates the excitation and emission sequence steps as follows: 1, excitation; 2, vibrational relaxation; 3 and 4, solvent relaxation; 5, fluorescence; and 6, vibrational relaxation.

wavelength) was obtained. This hypothesis agreed with the data shown in Table 2, which shows that the emission bands of the C_{60} solution in TCE commonly shifted to the higher wavelength. However, considering the dipole moments of the three solvents was only slightly different (compared to another polar solvent such water, which has a dipole moment of 1.87 D [64]); the reduction of the emission band was not large.

Theoretically, excitation occurs at shorter wavelengths or higher energy than the emission process. Conversely, emission generally appears at a longer wavelength than excitation. Moreover, both excitation and emission often appear to have a symmetric characteristic (mirror image rule) in which the distance between their two peaks is known as a stoke shift [18]. Therefore, the excitation and emissions spectra possessed by the C_{60} solutions in different solvents were combined, as shown in Figure 10. Two PL phenomena observed at wavelengths 430 to 470 nm and 650 to 850 nm were then confirmed to their absorption spectra.

As seen in Figure 10(a), the emission possessed by the C_{60} solutions in toluene and xylene at the wavelength of 420 to 480 nm had a symmetric characteristic with the excitation at wavelengths of 380 to 420 nm. The results of PL emissions were observable at wavelengths of 430 nm as a result of the electron transition of $S_0 \leftarrow S_1$ ($A_g \leftarrow T_{1u}$). The absorption spectra of the C_{60} solution in TCE are shown in a solid blue line in Figure 10(a); these spectra had a very large signal to noise (S/N) ratio. This excitation was possible due to the $\pi \rightarrow \pi^*$ transition. The $\pi \rightarrow \pi^*$ transition in C_{60} solution in TCE was weaker than that of the toluene and xylene solutions due to the absence of the benzene

ring in TCE. Thus, the PL intensity of the C_{60} solution in TCE weakened due to its lower solubility, as discussed previously. The absence of a PL peak at ~430 nm has also been reported for C_{60} in DMSO [66], which does not have a carbon hexagonal ring in its structure.

Unlike the phenomenon shown in Figure 10(a), in which the C_{60} solution in TCE had weak PL, the wider wavelength region in Figure 10(b) shows that the C_{60} solution in all three solvents had a significant PL peak that was well-observed. In Figure 10(b), the absorption (excitation) bands located at 450 to 650 nm had a mirror image with the emission bands located at 650 to 850 nm. However, the original emission intensity of the C_{60} solution in TCE before spectra normalization was considerably less, as shown in the original spectra in Figure 8(c) to (d). As discussed earlier, the excitation mechanism was predominantly derived from the solvents. The solvatochromism of C_{60} , which is a non-polar solute in non-polar solvents such as toluene and xylene, is commonly known to be solely dependent on dispersion forces influenced by the solvents' polarity, as indicated from their dipole moment. TCE had slightly higher dipole moments; that is, the emission band in TCE shifted to the longer wavelength, which is shown in Figure 8(f) and Figure 10(b). The C_{60} in toluene and xylene had almost closed emission bands at around 697 and 735 nm, labeled as P5 to P6 in Figure 8(f), respectively; however, the C_{60} in TCE had a shifted emission peak at 720 and 750 nm, labeled as P5' and P6' in Figure 8(f), respectively.

Correspondingly, PL spectroscopy has been found to better distinguish possible interactions between C_{60} and organic solvents with their different polarities than UV

Figure 10: The excitation and emission of C_{60} solution in different solvents at the wavelength range of: (a) 350 to 490 nm and (b) 450 to 850 nm.

absorbance spectroscopy. The C_{60} showed a significantly different emission peak when it interacted with TCE, the more polar of the non-polar solvents used in this study.

4 Conclusion

The solid C_{60} had different optical absorption characteristics compared to that of the dissolved C_{60} in organic solvents. The C_{60} solution in toluene, xylene, and TCE solvents generated excitation peaks at 404, 535, 570, 591, and 625 nm, which were slightly different from the excitation band energies of the solid C_{60} , as estimated by the Kubelka-Munk band gap calculations. Because of the higher solvent polarity of TCE, the C_{60} solution in TCE revealed a red-shift in which the PL emission peaks shifted to longer wavelengths as compared to C_{60} in toluene and xylene. The PL characteristics studied by spectroscopy better distinguished possible interactions between the C_{60} and organic solvents, with their different polarities, than did the characteristics studied by UV-Vis absorbance spectroscopy. Therefore, in future applications, due to its unique characteristics as an environment-sensitive fluorophore, C_{60} could be employed as a fluorescent probe to detect the solvent polarity effects, molecular

associations, and complex formation with polar and non-polar small molecules and macromolecules.

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