

Fluorescence of C₆₀ and Its Interaction with Pyridine

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Well-resolved strong fluorescence peaks for C₆₀ dissolved in pyridine in the range from 399 to 750 nm at room temperature are reported. These indicate that C₆₀ has important optical properties and great potential as a new photosensitive and luminescent material. In a C₆₀–pyridine solution, interaction between pyridine and C₆₀, which is further proved by the electroreduction of C₆₀ in pyridine as well as the surface-enhanced Raman scattering (SERS) spectrum of C₆₀, distorts the icosahedral symmetry of C₆₀. The relaxation of selection rules, due to the reduced symmetry of C₆₀ molecule, induces the observed strong fluorescence peaks.

Introduction

Since the discovery of fullerene, the photophysical properties of C₆₀ have been extensively studied.^{1–3} However, the fluorescence quantum yield of C₆₀ is very low, which is not only due to the intersystem crossing from singlet state to the excited triplet state, but also the forbidden electronic transitions between the excited singlet states and ground state.⁴ Therefore, it is difficult to observe strong fluorescence of isolated C₆₀ at normal experimental conditions.

However, the environmental effects, the rare gas matrix perturbation effect, and the low-temperature effect, for example, could relax the selection rules of C₆₀ and lead to a high fluorescence radiation rate.^{5–8} According to theoretical calculations, the lowest unoccupied molecular orbital in C₆₀ is threefold degenerate. Hence, C₆₀ could be able to accept up to six electrons during reduction, as an effective electron acceptor.^{8–11} With the electron donor, the possible formation of an adduct by charge transfer could lower the icosahedral symmetry of the C₆₀ molecule, leading to the observation of strong fluorescence of C₆₀. However, this is only theoretical speculation. The suitable adduct system, which could induce strong fluorescence of C₆₀, is difficult to acquire. Consequently, fewer results about the strong fluorescence of C₆₀ in room-temperature solutions have been reported. However, it is necessary to study the fluorescence spectrum and luminescence mechanism of C₆₀, as C₆₀ has the potential of being a new photosensitive and luminescent material. Recently, the report of C₆₀-based white light LED has stirred wide interest among researchers.¹²

In this paper, the fluorescence spectrum of C₆₀ in a room-temperature pyridine solution is observed. To the best of our knowledge, this is the strongest recorded fluorescence of C₆₀ in solutions at room temperature compared with the early reports.^{13,14} It is shown that formation of the C₆₀–pyridine adduct due to the interaction between C₆₀ and pyridine causes molecular reduction in symmetry of the C₆₀ molecule, which leads to the relaxation of selection rules and the induced high fluorescence radiation rate. Furthermore, we also prove that the C₆₀ molecule may make only a weak physical interaction with pyridine and does not substantively react chemically with pyridine.

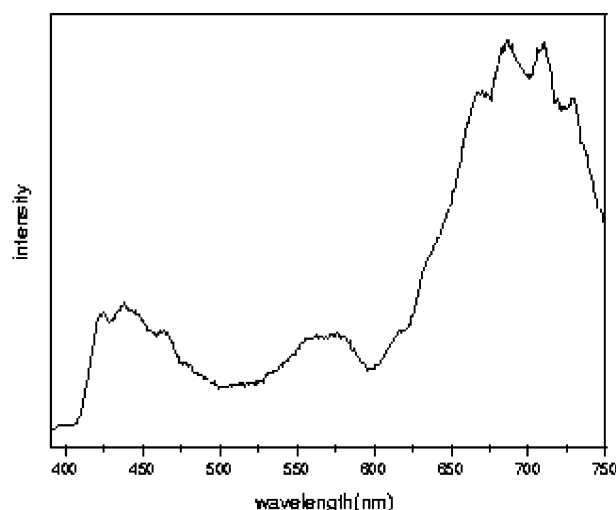


Figure 1. The fluorescence spectrum of C₆₀ in C₆₀–pyridine solution at room temperature with excitation at 380 nm.

Experiment

C₆₀ (99.9%) was dissolved in pyridine (HPLC grade), forming a brown solution. The electrolyte for the electrochemical experiment was (TBA)ClO₄.

Preparation of gold colloid: 75 mg KAuCl₄ was dissolved in 550 mL deionized water and the solution was heated to boiling. Next, 9 mL of a 1% aqueous solution of trisodium citrate was added to the boiling solution, accompanied with vigorous stirring. The mixed solution was kept boiling until it reached 200 mL.

The fluorescence spectra were recorded on a Fluorolog-3 spectrometer. The SERS spectra were obtained using an FT–IR spectrometer (RFS 100/s, Bruker). The electrochemistry measurements were carried out on the electrochemical working station. All of the measurements were performed at room temperature.

Results and Discussions

Figure 1 exhibits the fluorescence spectrum of C₆₀ in a C₆₀–pyridine solution, excited at 380 nm. There are three broad regions of fluorescence bands, centered at 425, 575, and 700

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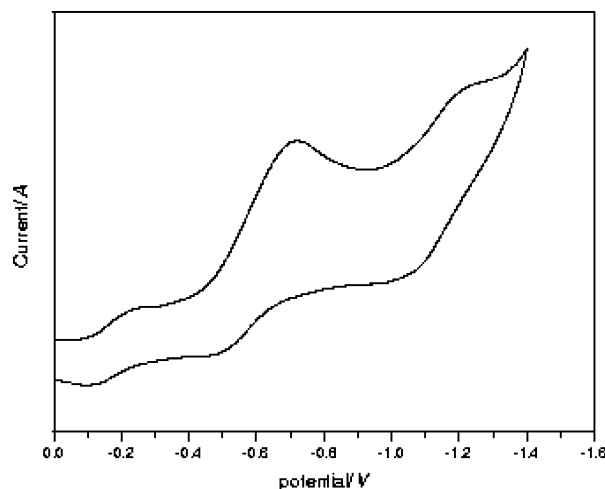


Figure 2. Cyclic voltammogram for the reduction of C₆₀ in pyridine containing 0.1 M (TBA)ClO₄ as a supporting electrolyte at room temperature. The counter and working electrodes were Pt, while Ag wire was used as the reference electrode. The scan rate was 100 mV/s.

nm, respectively. Among the three regions, the wide band centered at 425 nm includes four weak peaks: 399, 421, 435, and 465 nm. The band centered at 700 nm is also divided into several sharp peaks.

It is notable that the peaks shown in Figure 1 are not Raman peaks, because no frequency shift of the luminescence peaks was observed with different excitation wavelengths (such as 400 nm, etc.). Luminescence spectra have been reported for C₆₀ at very low temperatures.^{5–7} However, in room-temperature solutions, only weak fluorescence of C₆₀ was observed.^{13,14} It is most likely that this high-quality fluorescence spectrum should be attributed to the interaction between pyridine and C₆₀. This interaction could be further demonstrated by the following different experimental observations.

According to earlier reports,^{8–11,16} C₆₀ is an effective electron acceptor and pyridine is a potent electron donor. Therefore, charge transfer should exist in the C₆₀–pyridine system under certain conditions. Cyclic voltammetry was used to investigate the electrochemical reduction of C₆₀.^{8–11} Pyridine served as solvent and 0.1 M (TBA)ClO₄ served as a supporting electrolyte, respectively. The counter and working electrodes were both made of Pt, and Ag wire was used as the reference electrode. Three reduction peaks of C₆₀ are observed as shown in Figure 2, which indicates that charge transfer has occurred between C₆₀ and pyridine. In other words, C₆₀ molecules capture electrons from pyridine molecules. Similar to the fullerenes/*N,N*-diethylaniline charge-transfer complex,⁵ it is likely that C₆₀ and pyridine form an adduct through charge transfer. Sumant et al.¹⁷ also reported that C₆₀ formed a 1:1 charge–transfer complex with pyridine in CCl₄ by the absorption spectrometric method.

Surface-enhanced Raman scattering (SERS) spectra of C₆₀ in gold hydrosol, as indicated in Figure 3a, also illuminate the formation of the C₆₀–pyridine adduct. As is well known, C₆₀ has a low solubility in aqueous golden hydrosol and a low concentration in the mixed C₆₀–pyridine solution. However, the SERS spectrum with an enhancement factor of 8×10^4 shows that many C₆₀ molecules have successfully attached to the surface of gold particles.¹⁸ The C₆₀–pyridine adduct plays a crucial role in this process. Drawn by pyridine molecules owing to the formation of an adduct between C₆₀ and pyridine, the hydrophobic C₆₀ molecules could disperse in hydrosol and absorb onto the surface of gold nanoparticles.

It is notable that there is mainly weak physical interaction between C₆₀ and pyridine in the C₆₀–pyridine adduct, as was

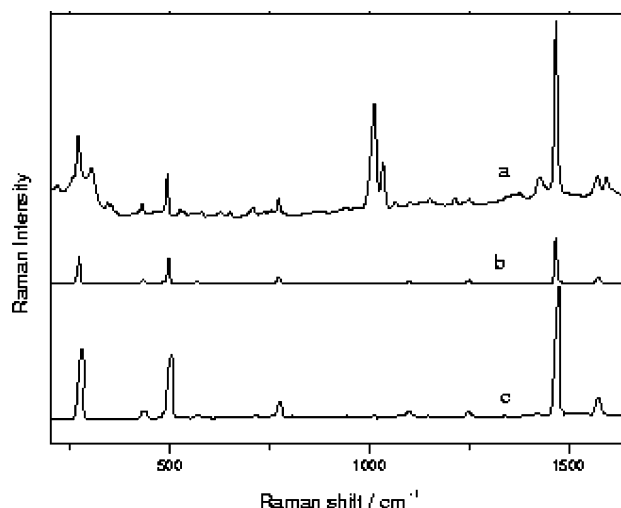


Figure 3. Raman and SERS spectra of C₆₀. (a) SERS spectrum of C₆₀ from C₆₀–pyridine solution mixed with gold hydrosol; (b) Raman spectrum of original pure solid C₆₀; (c) Raman spectrum of C₆₀ solid separated out from C₆₀–pyridine–solution.

proved through the following experimental result. The mixed C₆₀–pyridine solution was dropped onto the clean glass, then pyridine evaporated until C₆₀ was separated out and crystallized into a solid. The Raman spectrum of crystallized C₆₀ on the glass in Figure 3c shows the same result as that of the original pure C₆₀ solid in Figure 3b. This suggests that the C₆₀ molecule retains the complete fullerene structure of the original pure C₆₀ solid after being separated out from the pyridine solution. Therefore, the C₆₀ molecule probably makes only a weak physical interaction with pyridine and does not substantively react chemically with pyridine.

All of the above evidence indicates that there exists weak physical interaction between C₆₀ and pyridine through charge transfer. The fluorescence radiation rate is increased greatly, arising from symmetry lowering and selection-rule relaxing of C₆₀ induced by the formation of a C₆₀–pyridine adduct due to this interaction.

With respect to the 729 nm, 709 nm, 685 nm, and 668 nm peaks, similar to the analogy of M. Matus,¹⁹ we tentatively ascribe them to the recombination of the self-trapped exciton. The electrons could be excited from the valence band to the conduction band in the case of illumination. Because of the strong electron–vibration coupling, in some cases, the excited electrons and remaining holes would create a local deformation of the lattice and thus localize the electrons into a state below the conduction band and above the valence band (band gap).¹⁹ This kind of self-trapped exciton is apt to generate in systems with reduced dimensionality. Since the formation of an adduct between C₆₀ and pyridine leads to a reduction in symmetry and an increase in dimensionality of the C₆₀ molecule, the probability of a self-trapped exciton is comparatively reduced. The excited particles stay longer at the edges of the conduction band. They may recombine with the exciton complex or phonon replica, which results in the enhanced fluorescence radiation.

Fluorescence peaks may include the information of the vibrational mode symmetries of the ground state.^{20–22} Therefore, as far as the weak peaks at 399 nm (3.10 eV), 421 nm (2.94 eV), 435 nm (2.85 eV), and 465 nm (2.67 eV) are concerned, we believe that these four peaks reflect A_g and H_g modes of vibronic sidebands of C₆₀. This is because the separation in energy between adjacent peaks is 0.06 eV, 0.09 eV, and 0.18 eV, respectively. This is just coincident with the Raman spectra

at 496 cm^{-1} [0.06 eV, $A_g(1)$], 772 cm^{-1} [0.09 eV, $H_g(4)$], and 1469 cm^{-1} [0.18 eV, $A_g(2)$], respectively.²³

Conclusion

Strong fluorescence for C_{60} in a room-temperature pyridine solution is reported in the range from 399 to 750 nm. There are three main regions of fluorescence bands centered at 425, 575, and 700 nm, respectively. The weak physical interaction between pyridine and C_{60} , which is further proved by the electroreduction of C_{60} in pyridine as well as the surface-enhanced Raman scattering (SERS) spectrum of C_{60} , lowers the icosahedral symmetry of the C_{60} molecule. The relaxation of selection rules due to this reduction in symmetry of the C_{60} molecule induces the observed fluorescence. The peaks around 400 nm reflect the A_g and H_g modes of vibronic sidebands of C_{60} , and the fluorescence sharp peaks near 700 nm have been tentatively explained in terms of radiative recombination of the self-trapped exciton. Choosing an appropriate molecule to form fullerene adduct systems that could induce strengthened fluorescence of fullerene may offer a new approach for the fabrication of novel fullerene-based luminescent materials.

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References and Notes

(1) Cheng, J. X.; Fang, Y.; Huang, Q. J.; Yan, Y. J.; Li, X. Y. *Chem. Phys. Lett.* **2000**, 330, 262.

- (2) Pailt, D. K.; Spare, A. V.; Mittal, J. P. *Chem. Phys. Lett.* **1992**, 195, 1.
- (3) Arbogast, J. W.; Darmanyan, A. P.; Foote, C. S.; Rubin, Y.; Diederich, F. N.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Phys. Chem.* **1991**, 95, 11.
- (4) Ma, B.; Sun, Y.-P. *J. Chem. Soc., Perkin Trans. 2* **1996**, 2157.
- (5) Wang, Y. *J. Phys. Chem.* **1992**, 96, 764.
- (6) Heuvel, D. J.; Chan, I. Y.; Goren, E. J. J.; Matsushita, M.; Schmidt, J.; Meijer, G. *Chem. Phys. Lett.* **1995**, 233, 284.
- (7) Rice, J. H.; Aures, R.; Galaup, J. P.; Leach, S. *Chem. Phys. Lett.* **2001**, 263, 401.
- (8) Sassara, A.; Zerza, G.; Chergui, M. *J. Chem. Phys.* **1997**, 107, 8731.
- (9) Haymet, A. D. *Chem. Phys. Lett.* **1985**, 122, 421.
- (10) Chang, A. H. H.; Ermler, W. C.; Pitzer, R. M. *J. Phys. Chem.* **1991**, 95, 9288.
- (11) Meerholz, K.; Tschuncky, P.; Heinze, J. *J. Electroanal. Chem.* **1993**, 347, 425.
- (12) Luthi, H. P.; Almlof, J. *Chem. Phys. Lett.* **1987**, 135, 357.
- (13) Hutchison, K.; Gao, J.; Schick, G.; Rubin, Y.; Wudl, F. *J. Am. Chem. Soc.* **1999**, 121, 5611.
- (14) Kim, D.; Lee, M. *J. Am. Chem. Soc.* **1992**, 114, 4429.
- (15) Sun, Y. P.; Wang, P.; Hamilton, N. B. *J. Am. Chem. Soc.* **1993**, 115, 6378.
- (16) Dubois, D.; Moninot, G.; Kunter, W.; Jones, M. T.; Kadish, K. M. *J. Phys. Chem.* **1992**, 96, 7137.
- (17) Bhattacharya, S.; Banerjee, M.; Mukherjee, A. K. *Spectrochim. Acta, Part A* **2002**, 58, 2563.
- (18) Yang, X. C.; Fang, Y. *J. Phys. Chem. B* **2003**, 107, 10100.
- (19) Matus, M.; Kuzmany, H.; Sohmen, E. *Phys. Rev. Lett.* **1992**, 68, 2822.
- (20) Palewska, K.; Sworakowski, J.; Chojnacki, H. *J. Phys. Chem.* **1993**, 97, 12167.
- (21) Xia, A. D.; Pan, H. B.; Zhang, X. Y.; Fu, S. J.; Shi, J. Y.; Zuo, Jian.; Xu, C. Y. *J. Luminescence* **1995**, 63, 301.
- (22) Negri, F.; Orlandi, G.; Zerbetto, F. *J. Chem. Phys.* **1992**, 97, 6496.
- (23) van Loosdren, P. H. M.; van Benthum, P. J. M.; Verheijen, M. A.; Meijer, G. *Chem. Phys. Lett.* **1992**, 198, 587.