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Photochemical and Photophysical Properties of Three Carbon-Bridged Fullerene Dimers: C₁₂₁ (I, II, III)

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The photochemical and photophysical properties of the three C₁₂₁ isomers (I, II, III) were investigated with MADLI-TOF-MS, UV–vis spectra, fluorescence spectra, absorption spectra of their DMA complexes, and theoretical calculations. The three isomers of C₁₂₁ (I, II, III) have different stabilities under laser irradiation, but isomer I and isomer II show good stability against the heat-induced conversion between different isomers: No conversion between the isomers was found after heating the mixture of isomer I and isomer II at 353 K for 12 h in Ar atmosphere. The results of UV–vis absorption and fluorescence spectra indicate that interactions between two C₆₀ moieties of C₆₀=C=C₆₀ in the ground and singlet states are not significant, C₁₂₁ (I, II, III) behaves as an electron-acceptor similar to C₆₀. These indicate that the formation of the fullerene chain structure (e.g., C₆₀=C=C₆₀) does not disturb the photochemical and photophysical properties of the C₆₀ monomer itself, even that the properties were enhanced by the formation of the polymer. This is significant for the C₆₀ polymer in photochemical or photoelectronic applications in which C₆₀=C=C₆₀ can be an excellent basic unit of polymers.

Introduction

In recent years, considerable attention has been given to the modification and functionalization of fullerenes in which a series of fullerene polymers have been produced, such as C₁₂₀,¹ C₁₂₁,^{2–5} C₁₂₂,^{2,5,6} C₁₂₀O,^{7–9} C₁₃₁,^{4,10} C₁₄₁,^{11,12} C₁₂₂H₄,¹³ et al. In these fullerene chain structures, the dimer C₆₀=C=C₆₀ (C₁₂₀), the carbon-bridged dimer C₆₀=C=C₆₀ (C₁₂₁), the heteroatom-bridged dimer C₆₀–O–C₆₀ (C₁₂₀O), etc. could be used as the basic units. The research of the interaction between the fullerene cages is essential to the formation of one- or two-dimensional fullerene-based material and the exploration of their photochemical or photoelectronic properties is especially important for their applications in polymer science.^{14–17} For the heteroatom-bridged fullerene dimers such as C₁₂₀O⁸ or C₁₂₂H₄,¹³ the electronic interactions between the two fullerene cages were found to be strong and the C₆₀ cage was influenced by the other C₆₀ moiety.^{8,13} However, only a few studies are reported to elucidate the properties of the carbon-bridged fullerene dimer. The different electronic structure of the bridge atom might result in different properties for the polymer materials.

In this paper, we studied the photochemical and photophysical properties of three isomers of C₁₂₁ (I, II, III) in the ground and singlet states. The relative stability was compared from three aspects: their yield, their stability under laser irradiation, and their thermal stability.

Experimental Methods

C₁₂₁ was synthesized by neutron irradiation as described in the previous report.⁴ In brief, C₆₀, as the target, was irradiated for 2 h by neutron beams. The beam composition was the following: fast neutrons of $\sim 5.4 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$, thermal neutrons of $\sim 5.4 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$, and a fast-to-thermal neutron flux ratio of about 10%. The samples were then measured for 3000 s by using a high-purity germanium detector (HPGe) to ensure no radioactivity was detected.

Separation and isolation of the three isomers were performed by using high-performance liquid chromatography (HPLC, LC908-C60, Japan Analytical Industry Co.) with 5PBB (Nacalai Co. Japan, 20 × 250 mm) and Buckyprep columns (Nacalai Co. Japan, 10 × 250 mm). The mass spectra were measured with the Matrix-Assisted Laser Desorption and Ionization Time of Flight MS (MALDI-TOF-MS, AutoFlex, Bruker Co., Germany). 9-Nitroanthracene was used as the matrix.

Steady-state absorption spectra in the UV–vis regions were measured with a TU-1901 UV–vis spectrophotometer (Beijing Perkinje General Instrument Co., Ltd, China).

Steady-state absorption spectra of the C₁₂₁ (I, II, III)–DMA (*N,N*-dimethylaniline, electron donor) system in toluene in the Vis-NIR region were measured with a UV-3100, UV–Vis-NIR Recording Spectrophotometer (Shimadzu, Japan).

Steady-state fluorescence spectra were measured on a FLS920 combined with a Steady State and Lifetime Spectrometer (Edinburgh Instrument Ltd, England).

The structures of the three isomers were calculated by using the Gaussian 98W package and their molecular orbitals were optimized by B3LYP/6-31G*.

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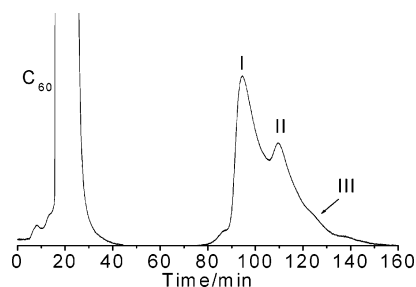


Figure 1. HPLC chromatogram of the mixture by neutron irradiation separated with 5PBB column (20 × 250 mm), toluene, 12 mL/min, 330 nm detection.

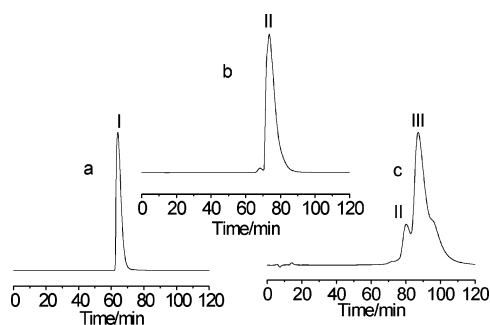


Figure 2. (a–c) HPLC chromatograms of isomer I (a), isomer II (b), and isomer III (c) separated with buckyprep column (10 × 250 mm), toluene, 1.6 mL/min, 330 nm detection.

Results and Discussion

1. Separation, Mass Spectra, and Stability of the Three Isomers of C_{121} (I, II, III). After C_{60} was irradiated by neutrons in the reactor and no radioactivity was detected, the sample was dissolved in toluene under air atmosphere and separated by HPLC coupling on a 5PBB column with toluene as the mobile phase. The HPLC chromatogram is shown in Figure 1. From the HPLC spectrum, we can see that, besides C_{60} , there were three new peaks, whose retention times (T_R) was 94.8, 109.8, and 123.6 min, respectively. The three fractions were then isolated by HPLC coupling with the Buckyprep column. Figure 2a–c shows the HPLC of the three purified fractions. The MALDI-TOF-MS spectra indicated that they were the three isomers of C_{121} (m/z 1453.2) (Figure 3a–c). Therefore, they were assigned to be C_{121} -I (fraction I), C_{121} -II (fraction II), and C_{121} -III (fraction III), respectively. The purity of isomers I and II was >99% and the purity of isomer III was about 85%.

The relative yield of the three isomers could be seen from Figure 1. The yield of isomer I was the highest whereas the yield of isomer III was the lowest among the three isomers. The formation of C_{121} succeeded under a severe neutron irradiation condition and the decomposition of C_{121} could also happen at the same time; therefore, the yield should be totally dependent on their thermodynamic stability. The theoretical simulation indicated that isomer I was the most stable whereas isomer III was the most unstable if just considering their thermodynamic stability.¹⁸ However, it was difficult to produce isomer I by using general methods, such as grounding,³ perhaps because a higher energy barrier might be overcome to form isomer I, compared with that of isomer II.

Though the HPLC spectra showed that the samples were in high purity (Figure 2), it was not possible to get a single peak by MS because they dissociated under laser irradiation.^{2,4,12,19} Compared their MS spectra shown in Figure 3a–c, which were measured under the same condition, we found that the peak heights of C_{121} and the main decomposed fragments were much

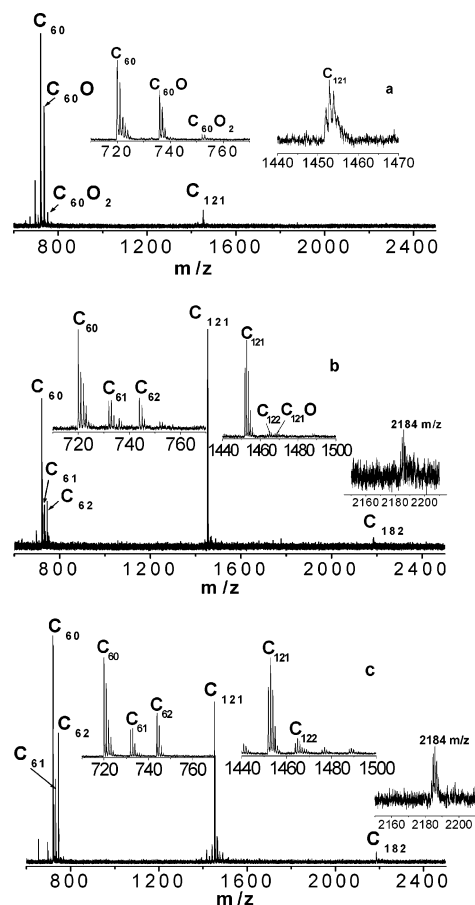


Figure 3. (a–c) MALDI-TOF MS of isomer I (a), isomer II (b), and isomer III (c). The insertions are the enlarged spectra of C_{121} and fragments (negative ionization, reflection mode, and 9-nitroanthracene as matrix).

different. The main peak in the spectrum of isomer I corresponded to C_{60} and the peak height of C_{121} was very low (Figure 3a). As for isomers II and III, the peak height of C_{60} was similar to that of C_{121} ; their difference was that the peak height of C_{121} was a little bit higher than that of C_{60} in the spectrum of isomer II, but lower than that of C_{60} in the spectrum of isomer III.

Besides C_{60} , the decomposed fragments of the three isomers under the laser irradiation were also different from each other. C_{60} was the main decomposed fragment and no C_{61} and C_{62} were detected in isomer I, which indicated that isomer I was easier to decompose to C_{60} cages. C_{60} , C_{61} , and C_{62} could be seen obviously in the MS spectra of isomers II and III, which indicated that they were easier to decompose to C_{60} and C_{61} , and consequently C_{62} was formed under the laser condition. Furthermore, we also found a peak (m/z 2184) in both of the spectra of isomers II and III, which corresponds to C_{182} , but we not find it in the spectrum of isomer I. It was speculated to be formed with the C_{61} fragment of isomers II and III and C_{121} itself. That is to say, under laser irradiation, different isomers gave different dissociated fragments.

In isomer I, the central bridged carbon atom was connected to the two cages by two cyclopropane structures. The bands were strongly strained and were easily broken under laser irradiation. Shimotani et al. pointed out that the strain energy of isomer I was the biggest among the three isomers,¹⁸ which was the reason why isomer I was easier to decompose to C_{60} under laser condition. In isomers II and III, both had the

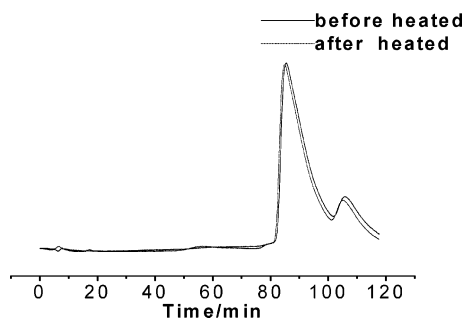


Figure 4. HPLC chromatograms of the mixture of isomers I and II before and after heating (5PBB column (20 × 250 mm), toluene, 12 mL/min, 330 nm detection).

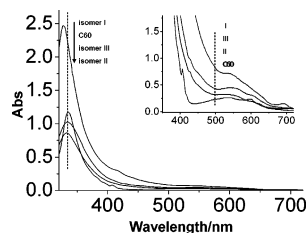


Figure 5. UV-vis spectra of C_{60} , isomer I, isomer II, and isomer III in toluene and enlarged spectra from 350 to 720 nm (insert).

homofullerene structure, therefore, C_{61} , C_{62} , and C_{182} appeared in their mass spectra.

The thermal stability of isomers I and II was further determined by heating their mixture at 353 K for 12 h under Ar atmosphere. The heated solution was rechromatographed by HPLC, but no other fraction was found except for the two isomers (Figure 4), which confirmed that isomers I and II were stable enough to resist the heating under Ar atmosphere. In past experiments, fullerenes (except for $C_{61}H_2$) could be thermally converted to methanofullerenes.^{21–28} For instance, Diederich,^{26,27} Osterodt,²⁸ Prato,²³ and Smith²⁴ have reported quantitative isomerization of apically substituted C_{60} -derived [5,6] fullerenes to the corresponding [6,6] cyclopropane upon thermolysis in toluene, and Prato pointed out that it was required that the methane carbon carried substituents in the photochemical conversion of fulleroid via a di- π -methane mechanism to the corresponding methanofullerene.²³ In accord with these observations, Smith concluded that apical substitution was required for facile thermal isomerization.²¹ However, isomers I and II of C_{121} behaved much differently. They were more stable under our condition. The reasonable explanation was that more energy was necessary to conquer the spacial resistance in the conversion among the isomers, because the substituent was the big C_{60} cage compared with other substituted C_{60} -derived [5,6] fullerenes.

2. Ground and Singlet States of the Three Isomers of C_{121}

Figure 5 shows the UV-vis spectra of the three isomers of C_{121} and C_{60} . The spectrum of C_{60} showed an absorption band at 334 nm with broad bands around 600 and 530 nm. The spectra of the three isomers were quite similar and similar to that of C_{60} , but the absorption bands showed a slight shift with each other. The spectrum of isomer I showed absorption bands at 691, 425, and 327 nm. The spectrum of isomer II showed absorption bands at 690, 425, and 333 nm, whereas that of isomer III showed an absorption band at 334 nm. All of them showed broad bands around 600 and 530 nm. As is well known, there are 60 π electrons in fullerene C_{60} , and there are 58 and 60 π electrons in the methanofullerene and homofullerene, respectively. Isomer I is composed of two methanofullerenes, isomer III is the combination of two homofullerenes, and isomer

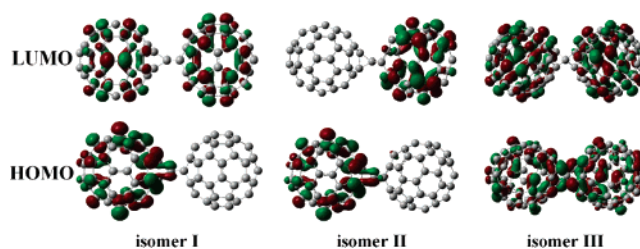


Figure 6. Molecular orbitals of HOMO and LUMO of the three isomers.

TABLE 1: The Orbital Energy of the Three Isomers of C_{121} (in hartrees)

isomer	HOMO	LUMO	HOMO-LUMO
I	−0.215	−0.119	−0.096
II	−0.212	−0.121	−0.091
III	−0.216	−0.120	−0.096

II contains both of them. Therefore, the spectrum of isomer III was almost identical with that of C_{60} , whereas the spectrum of isomer I exhibited a hypsochromic shift (from 335 to 327 nm) and a new absorption band at 691 nm, which was identical with those of methanofullerenes.^{19–21,28–30} Isomer II could be considered to be the mixture of isomer I and isomer III. As a result, isomer II had both characteristics of isomer I and isomer III, which agreed well with the previous report.³¹

Actually, C_{121} -I, -II, and -III are the only possible connections for carbon-bridged C_{121} isomers due to the high symmetry of the C_{60} cage: [6,6]-[6,6], [5,6]-[6,6], and [5,6]-[5,6].¹⁸ In C_{121} -I, the center carbon and four bridgehead carbons are all sp^3 atoms; in C_{121} -II, the center carbon and two bridgehead carbons are sp^3 atoms, while the other two bridgehead carbon atoms are sp^2 ; in C_{121} -III, only the center carbon atom is sp^3 , and all four of the bridgehead carbons are sp^2 atoms. These can be identified from the NMR measurement. These isomers are soluble in toluene, whose solubility is enough for HPLC isolation. Nevertheless, their solubility in available NMR solvents is quite low. We tried several different types of available solvents to increase the C_{121} concentration for NMR measurements, and only obtained the ^{13}C NMR spectrum for isomer I, which is similar to that reported in ref 2. Because of the lower solubility of isomers II and III, it was impossible so far to gain a qualified spectrum with high signal-to-noise for these two isomers.

The molecular orbital calculation^{32,33} of the three isomers is shown in Figure 6 and Table 1. From the calculation, the HOMO electron densities of isomers I and II were localized on the methanofullerene moiety, while part of the LUMO's electron density of isomer I and all of LUMO's electron density of isomer II were localized on the homofullerene moiety, and there also existed different electron density between LUMO's and HOMO's of isomer III.¹⁸ Therefore, the lowest electronic transitions of the three isomers were expected to generate a CT-type excited state, which should show an absorption band in the longer wavelength region. Since there were no longer wavelength absorption bands in the spectra of the three isomers and little overlap between the two cages from the molecular orbital calculation, the electron transition could be neglected. Different from the heteroatom-bridged dimers, the carbon-bridged dimers maintain more features of fullerene and the cages are more independent of each other, indicating that the carbon-bridged polymers possess similar properties to those of fullerenes.

Figure 7 showed the emission spectra excited at 580 (Figure 7a) and 312 nm (Figure 7b) and the excitation spectra probed at 686 nm (Figure 7c) at room temperature. It was found that

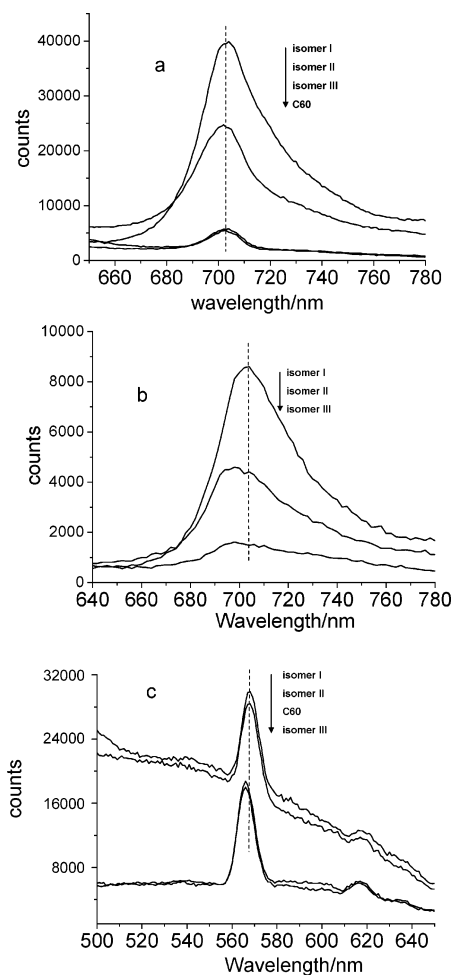


Figure 7. (a–c) Fluorescence emission spectra (excited at 580 (a) and 312 nm (b)) and excitation spectra (probed at 686 nm) of C_{60} , isomer I, isomer II, and isomer III in toluene.

the tendency of emission intensity was similar to those of the absorbance of the three isomers and C_{60} as the excitation energy was increased in a range from 500 to 650 nm. The luminescence maxima were located in the excitation range of 550–580 nm, which was consistent with the strong absorption in this region exhibited by the fullerene cage. It suggested a mechanism whereby the excitation energy was absorbed by the fullerene cage. Upon excitation with 580 nm light, C_{60} and the three isomers of C_{121} showed similar fluorescence bands around 704 nm (Figure 7a), which were similar to those of $C_{61}H_2$,^{30,34} C_{120} ,^{29,35} $C_{120}O$,³⁶ and other fullerene derivatives.^{28,37} The molecular orbital calculations supported the similarity. However, a small difference was found between the emission of the three isomers and C_{60} . For instance, no luminescence can normally be detected at room temperature in C_{60} solution. The weak fluorescence emission centered at 700 nm would be ascribed to C_{60} microbulk in our supersaturated solution.^{38,39} However, the three isomers of C_{121} were not saturated and their concentrations were hundred of times lower than that of the C_{60} sample, whereas their fluorescence intensity was higher than that of C_{60} , which should be responsible for the lower symmetry of the C_{121} compared with C_{60} . Similar fluorescence response was also obtained under excitation at 312 nm (Figure 7b).

Comparison of both the absorption and fluorescence spectra among the three C_{121} isomers and C_{60} suggested that there were no significant interactions between the two C_{60} moieties in the ground and singlet states. It is understandable because the central bridged carbon atom of C_{121} is connected with the two C_{60} cages

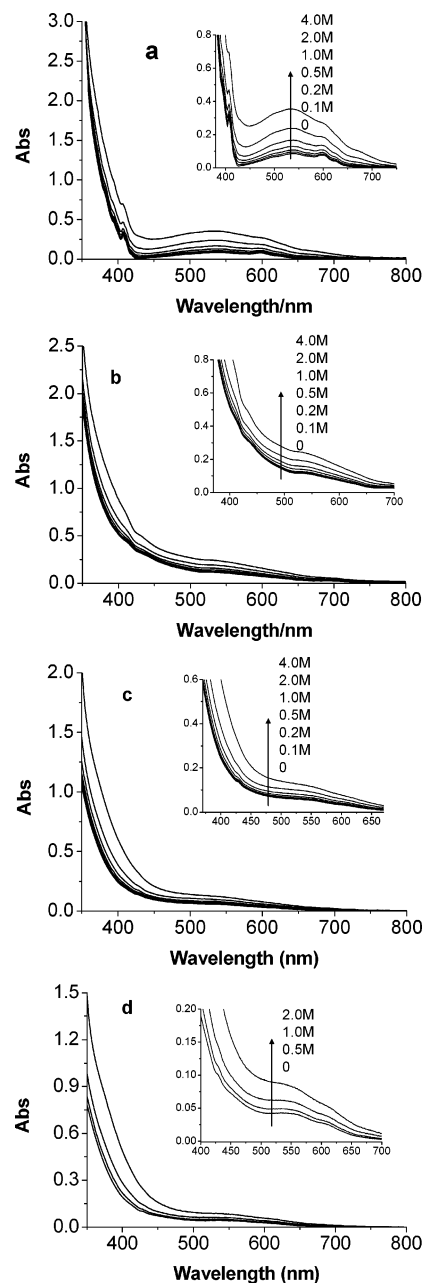
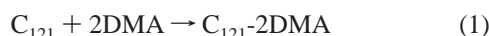


Figure 8. (a–d) Absorption spectra of C_{60} (a), isomer I (b), isomer II (c), and isomer III (d) in the presence of DMA at various concentrations in toluene.

by four σ bonds and there are no electron pairs to form the π band, which is very different from that of $C_{120}O$.^{8,9} Additionally, the difference in the absorption spectra among the three isomers and C_{60} was mainly due to the partial breakage of the π -orbital system. However, because of the lower symmetry of C_{121} , it was easier to generate the excited state especially for isomer I and isomer II. Therefore, the carbon-bridged dimers not only possess similar properties to those of fullerene but also had more potential to be used as optical and electronic devices.⁴⁰

3. Complexes of the Three Isomers of C_{121} in the Ground State. C_{60} has been proved to be a good electron acceptor in the ground states. The electrochemical measurement of C_{121} indicated that the first reduction potentials for C_{60} and isomer II were almost identical.³ The charge transfer played an important role in fullerene's optical and electronic applications. Here, we investigated the charge transfer between the three isomers of C_{121} and *N,N*-dimethylaniline (DMA), which was used as an electron donor. Figure 8a–d showed the absorption

spectra of the DMA complexes of C₁₂₁ and C₆₀ in the ground state. The result of C₆₀-DMA complexes was in agreement with early reports.^{41,42} The absorption of the broad band around 500–600 nm was increased with the increase of the concentration of DMA, the absorption intensity of the three isomers of C₁₂₁ became stronger too, and there was no new band emerging, indicating the C₁₂₁ formed charge-transfer complexes with DMA but the interaction was weak, similar to that of C₆₀. Sun et al.⁴² reported that C₆₀ and DMA could only form the 1:1 complex. Since C₁₂₁ was a similar electron acceptor with C₆₀ and the two cages could be reduced at the same time, we speculated that C₁₂₁ could form the 1:2 complex with DMA.



C₆₀, as a good electron acceptor, has been used to enhance the photovoltaic conversion efficiency in polymer photovoltaic cells,^{17,43,44} and because C₁₂₁ possesses similar photophysical and photoelectronic properties as C₆₀ and is also proven to be a good electron acceptor, it is feasible that C₁₂₁ can be used as a basic unit in polymer photovoltaic cells.

Conclusions

In this paper, we presented the photophysical and photochemical properties of all three C₁₂₁ isomers (I, II, III) and their stability at different conditions. The dissociation of three isomers yielded different fragments under the same laser condition. However, isomers I and II were thermally stable and no conversion between them was observed by heating them at 353 K for 12 h under Ar atmosphere. The UV–vis spectra and the theoretical calculation indicate that the C₆₀ cage is nearly independent so that the carbon-bridged polymer (C₆₀=C=C₆₀) possesses properties similar to those of fullerenes. The fluorescence spectra of the three isomers show higher fluorescence intensity than C₆₀, implying that they possess better optical and electronic properties compared to those of C₆₀. The three isomers of C₁₂₁ were proved to be good electron acceptors and could form a 1:2 complex with DMA in toluene, which could be used as a basic unit in polymer photovoltaic cells.

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