Photophysical properties of multiply phenylated C\textsubscript{70} derivatives: Spectroscopic and quantum-chemical investigations

P.-F. Coheur\textsuperscript{a})
Laboratoire de Chimie Physique Moléculaire, Université Libre de Bruxelles, CP 160/09, 50 av. F. D. Roosevelt, B-1050 Brussels, Belgium

J. Cornil\textsuperscript{a}) and D. A. dos Santos
Service de Chimie des Matériaux Nouveaux, Centre de Recherche en Electronique et Photonique Moléculaires, Université de Mons-Hainaut, Place du Parc 20, B-7000 Mons, Belgium

P. R. Birkett
Fullerene Science Centre, CPES School, University of Sussex Brighton, BN1 9QJ, United Kingdom

J. Liévin
Laboratoire de Chimie Physique Moléculaire, Université Libre de Bruxelles, CP 160/09, 50 av. F. D. Roosevelt, B-1050 Brussels, Belgium

J. L. Brédas
Service de Chimie des Matériaux Nouveaux, Centre de Recherche en Electronique et Photonique Moléculaires, Université de Mons-Hainaut, Place du Parc 20, B-7000 Mons, Belgium and Department of Chemistry, The University of Arizona, Tucson, Arizona 85721-0041

D. R. M. Walton, R. Taylor, and H. W. Kroto
Fullerene Science Centre, CPES School, University of Sussex Brighton, BN1 9QJ, United Kingdom

R. Colin\textsuperscript{b)}
Laboratoire de Chimie Physique Moléculaire, Université Libre de Bruxelles, CP 160/09, 50 av. F. D. Roosevelt, B-1050 Brussels, Belgium

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The photophysics of six multiply phenylated C\textsubscript{70} derivatives [C\textsubscript{70}Ph\textsubscript{2}, C\textsubscript{70}Ph\textsubscript{4}, C\textsubscript{70}Ph\textsubscript{6} (two regioisomers), C\textsubscript{70}Ph\textsubscript{8} and C\textsubscript{70}Ph\textsubscript{10}] have been investigated by means of steady state spectroscopy in cyclohexane solution and quantum-chemical calculations derived from semiempirical Hartree–Fock approaches. There is good agreement between the measured absorption spectra and the INDO/SCI calculated excitation energies for each derivative. The foregoing results and some additional ground state properties calculated at the AM1 level have been used to predict that the perturbation of the π electronic system of the cage results in significant changes in the photophysics of the fullerene derivatives. The effects of conjugation and spatial localization of the HOMO and LUMO orbitals on the energy of the first electronic transition are discussed in greater detail. © 2000 American Institute of Physics.

INTRODUCTION

Fullerenes C\textsubscript{60} and C\textsubscript{70} possess many interesting properties including remarkable nonlinear optical behavior and ability to sensitize oxygen upon photoexcitation. These properties, which rely on the photophysical characteristics of the molecules,\textsuperscript{1} have produced opportunities for their use as optical limitters\textsuperscript{2} or photodynamic agents.\textsuperscript{3,4} The discovery that C\textsubscript{60} and C\textsubscript{70} are chemically reactive has considerably widened the field of potential applications to include new classes of functionalized molecules, all of which have specific properties that require characterization. Indeed, as the functionalization of the fullerenes requires addition to C–C double bonds, it is expected that the resulting derivatives have photophysical properties different from those of the parent molecule. Extensive studies of monofunctionalized C\textsubscript{60} derivatives have, however, shown these molecules to retain most of the spectral signatures of C\textsubscript{60}.\textsuperscript{1,5–17} In contrast, very few studies examined the photophysical behavior of multifunctionalized fullerene derivatives\textsuperscript{7,8,18–24} (especially derivatives of C\textsubscript{70} and higher fullerenes). Such multifunctionalization initiates a larger perturbation of the cage π electronic system and, as a result, the molecules may exhibit more unusual optical properties compared to those of the parent and monofunctionalized fullerenes. In another paper, we described the spectroscopic properties of five hexafunctionalized C\textsubscript{60} derivatives, which differ only in their functional groups or their geometrical configurations.\textsuperscript{25} As a result of the geometric and electronic changes to the fullerene cage in the foregoing molecules, significant modifications of both the ground and excited states with respect to C\textsubscript{60} were observed. These results, however, lead us to conclude that the nature of the addends/substituents has, in these examples, little effect on the spectroscopic properties of the molecules, even though there are significant changes to their one-electron properties.
EXPERIMENTAL AND THEORETICAL METHODS

Synthesis

The detailed syntheses and characterization of the C_{70}Ph_8 and C_{70}Ph_{10} samples have been published previously.\textsuperscript{26} Similar data on the other C_{70}Ph_{2n} derivatives will be the object of a forthcoming paper.\textsuperscript{27}

Spectroscopic measurements

A small quantity of each material was dissolved in cyclohexane (spectroscopic grade); concentrated (\textasciitilde 10^{-4} mol l^{-1}) and dilute solutions (\textasciitilde 10^{-6} mol l^{-1}) were prepared. Due to the small amount of material available, the concentration of these solutions were not more precisely determined. Absorption spectra were recorded with a HP 8452A spectrophotometer in the 210–820 nm spectral range by increments of 2 nm. The concentrated and dilute solutions of each derivative were used to record their absorption spectra in the visible and the UV region, respectively. Fluorescence spectra of each of the more concentrated solutions were recorded with a Shimadzu RF-5001PC spectrofluorophotometer.

Quantum-chemical calculations

The structure of each derivative was deduced using NMR spectroscopy. The structures presented for C_{70}Ph_2 and C_{70}Ph_4 are the predicted, preferred isomers (of a total of four and three, respectively) which satisfy the experimental data\textsuperscript{27} while both of the possible regioisomers of C_{70}Ph_6 which fit the NMR data\textsuperscript{27} are considered. Using these structures, the nuclear coordinates of each derivative were generated at the molecular mechanics level using the universal force field method.\textsuperscript{28} Adopting the latter coordinates as a starting point, the geometries of the derivatives were further optimized at the semiempirical Hartree–Fock Austin Model 1 (AM1) level,\textsuperscript{29} as implemented in the GAUSSIAN 94 package.\textsuperscript{30}

As in our study of the hexa-functionalized C_{60} derivatives,\textsuperscript{25} the AM1 calculated ground-state properties we pay most attention to in this paper are the heat of formation, the atomic charge distribution as obtained by a Mulliken population analysis,\textsuperscript{31} the ionization potential (f) and electron affinity (A) approximated by Koopmans theorem.\textsuperscript{32} The graphical representations of the HOMO and LUMO orbitals (graphical interface Insight II of Molecular Simulations Inc.)\textsuperscript{33} and their spatial localization, expressed in term of the participation number PN,\textsuperscript{34} are obtained on the basis of the LCAO coefficients calculated at the INDO/S level. Within this formalism, the PN writes (e.g., Refs. 25 and 35):

$$PN = \frac{\sum_{\lambda} c_{i\lambda}^2}{2\sum_{\lambda} c_{i\lambda}^4},$$

where $c_{i\lambda}$ is the LCAO coefficient on the $\lambda$th atom in the $i$th molecular orbital.

The fundamental electronic configurations of the phenylated C_{70} derivatives are all closed-shell systems, defining an electronic ground state of singlet multiplicity $S_0$. In the following, we only consider the electric dipole allowed transitions from $S_0$ to the manifold of electronic excited singlet states $S_n$, which are expected to dominate the absorption spectrum in the UV and the visible. The calculations of the vertical $S_0$–$S_n$ excitation energies and oscillator strengths are performed using the semiempirical Hartree–Fock INDO/S method\textsuperscript{36} and a single configuration interaction (SCI) technique. The Mataga–Nishimoto potential\textsuperscript{37} is used to express the electron interaction terms. The early INDO/SCI calculations of Bendale \textit{et al.}\textsuperscript{38} on C_{60} and C_{70} have shown the adequacy of this theoretical approach for the modeling of the absorption spectra of fullerenes in the visible and UV regions up to 5 eV. Above this energy limit, the calculated oscillator strengths were markedly underestimated with respect to the experimental data. Similarly an upper limit is to be expected for the present INDO/SCI calculations\textsuperscript{39} and we have therefore chosen to consider only the electronic transitions with energies lower than 5 eV. By analogy with our study on the C_{60} derivatives,\textsuperscript{25} we have included a maximum of 5625 excited configurations in the calculations (this number corresponds to all single excitations from the 75 highest occupied to the 75 lowest unoccupied MOs). The resulting data, which constitute a “bar spectrum” (vertical excitation energies vs oscillator strengths) are used to analyze the absorption spectra in the present work. To more adequately model the observed spectra over the entire spectral range, we also use a “synthetic spectrum,” obtained by convoluting the “bar spectrum” with a Gaussian function of given full width at half-maximum (FWHM).
FIG. 1. Schlegel diagrams giving the geometric configuration of the $C_{70}Ph_n$ derivatives ($n = 1$ to 5). The black balls represent the phenyl groups and the heavy black line represents the single C–C bonds involving a $sp^3$ carbon atom of the $C_{70}$ cage.
RESULTS

Geometry

The geometric configuration of the phenylated derivatives is visualized with the help of Schlegel diagrams in Fig. 1. The numbering of the cage carbon atoms is that adopted by IUPAC. Each molecule is at first glance characterized by a plane of symmetry; however, the phenyl groups are in fact not oriented symmetrically with respect to one another in their lowest energy conformations. The configuration of the molecules under study is therefore rather that of a pseudo-C_{s} symmetrical type. In the case of C_{70}Ph_{6}, it should be noted that although both regioisomers depicted in Fig. 1 fit the NMR data, and that isomer 2 is the preferred thermodynamic product, the structure shown as isomer 1 is considered to be the most likely for the derivative due to the favorable addition mechanism underlying its formation.

As a result of the weaker strain required for closure of the carbon cage of C_{70} compared with that of C_{60}, it is well known that the delocalized character of the electronic system is higher in the former molecule. This is confirmed, for example, by the existence of bonds of intermediate length on the C_{70} cage. By analogy to the AM1 calculated bond lengths (d) for C_{70}, we consider for the phenylated derivatives under study: (i) single bonds (with d>1.43 Å); (ii) intermediate bonds (for which 1.387≤d≤1.43 Å); and (iii) double bonds (with d<1.387 Å). A simple method of specifying the distinctive bonding for each multiply phenylated derivative consists then in listing and counting the bonds that belong to the above-defined groups (see Table I). In Table I, the single C–C bonds have been further subdivided into two classes: those single bonds which result from the presence of sp^{3} carbon atoms (for which d>1.50 Å) and those implying the presence of sp^{2} carbon atoms, respectively. It is observed, from the data presented in Table I, that the number of bonds involving sp^{3} carbon atoms increases linearly with the number of attached groups. In contrast, no such regularity can be distinguished within the other classes of bonds as one moves from one derivative to the next. This is especially true for the number of bonds which are of intermediate length and which can be considered, to a first approximation, as a measure of the degree of conjugation of the electronic system on the cage. From Table I, therefore, it can be noted that the predicted C_{70}Ph_{6} isomer (isomer 1) and C_{70}Ph_{10} are, respectively, the most and the least conjugated derivative. All of the other derivatives analyzed fall between these two extreme cases, including C_{70}, which we have used as a reference. It should be noted that electronic conjugation over the entire cage is necessarily limited for C_{70}Ph_{10} because of the presence of the sp^{3} carbon atoms that isolate two π electronic systems from one another (see Fig. 1).

Ground-state properties

The heats of formation calculated at the AM1 level are given in Table II. As the molecules have similar chemical composition the calculated values should, in principle, be consistent throughout the C_{70}Ph_{2n} series and should therefore allow a stability sequence to be established. The results reveal that the heat of formation increases with the number of phenyl groups attached to the C_{70} cage with a step-like evolution. C_{70}Ph_{2} and C_{70}Ph_{4} are characterized by a similar ∆H_{f} value of 1111±1 kcal mol^{-1}, which is larger than that of C_{70} (1061 kcal mol^{-1}) but smaller than that of C_{70}Ph_{6} isomer 1 and C_{70}Ph_{8} (1154±2 kcal mol^{-1}). The latter value is in turn smaller than that of C_{70}Ph_{10} (1185 kcal mol^{-1}). Only isomer 2 of C_{70}Ph_{6} lies slightly off sequence; its calculated heat of formation (1145 kcal mol^{-1}) confirms that it is more stable than the predicted structure of isomer 1.

The net atomic charges reported in Table II, which are obtained by a Mulliken population analysis within the AM1 formalism, are summed over the phenyl groups (the average value per phenyl is given for each derivative) and the C_{70} cage. The phenyl groups are in all of the investigated cases electron-donating with respect to the cage, as was also reported for phenylated C_{60} derivatives. Furthermore, the calculations indicate that the electron-donating character per phenyl group diminishes as the number of such groups attached to the fullerene cage increases. For example, the mean value per phenyl group is calculated to be +0.044 |e| in C_{70}Ph_{3} and +0.029 |e| in C_{70}Ph_{10}. The total charge donated to the cage is however a maximum for C_{70}Ph_{10} (+0.292 |e|) and, interestingly, one can show that the charge excess is redistributed similarly over the two independent π electronic subgroups defined above in this derivative.

The graphical representation of the HOMO and LUMO and their corresponding PN are given in Fig. 2. From Fig. 2 it can be seen that HOMOs and LUMOs differ strongly within the series of derivatives. For example, the HOMOs of C_{70}Ph_{8} and the C_{70}Ph_{6} isomers are localized on the cage (with a PN of about 31) whereas those of C_{70}Ph_{2}, C_{70}Ph_{4}, and C_{70}Ph_{10} are more strongly delocalized (PN of 47.3, 48.7, and 50.9, respectively) and do not necessarily involve the same carbon atoms. The same results are observed for the LUMOs. For both HOMOs and LUMOs, we note that the phenyl groups make little contribution.

The AM1 and INDO ionization potentials (I) and electron affinities (A) calculated within Koopman’s theorem are given in Table II. The AM1 HOMO and LUMO energy levels (E_{HOMO} = −I and E_{LUMO} = −A) are further represented on a scaled diagram (Fig. 3) in order to display the HOMO–LUMO energy difference (∆E = I−A) and the deviations with respect to the energy levels calculated for C_{70}. The AM1 results show that with the exception of the LUMO of C_{70}Ph_{2}, all other molecular orbitals are somewhat destabilized with respect to those in C_{70}. The HOMO and LUMO are, however, not destabilized by a similar amount as one moves down the series of C_{70}Ph_{2n} (increasing n) and, as a consequence, ∆E has values ranging from 4.90 eV for C_{70}Ph_{6} isomer 1 to 7.07 eV for C_{70}Ph_{10}. The INDO/S data yield a similar pattern although notable differences are obvious in the absolute orbital energy values as in the destabilization energies calculated with respect to C_{70} (see Table II).

Spectroscopic properties

The absorption and fluorescence spectra of each derivative dissolved in cyclohexane are given in Fig. 4; the corresponding spectra recorded for C_{70} are shown for the sake of...
One should note that for some derivatives the fluorescence spectrum reveals more than a single band. The bands lying to the red side of the fluorescence maximum are likely to be vibrational components of the $S_1\rightarrow S_0$ electronic transition and are accordingly also reported in Table III. On the other hand, we have disregarded the very weak features that are observed in some cases to the blue side of the fluorescence maximum as these bands originate probably from traces of other C$_{70}$Ph$_{10}$ molecules in the sample. We note finally that the fluorescence spectra recorded for C$_{70}$Ph$_8$ and C$_{70}$Ph$_{10}$ in cyclohexane at room temperature are in good agreement with the fluorescence measurements made by Groenen et al. for the molecules in decalin/cyclohexane at 4.2 K.41

For C$_{70}$Ph$_2$, C$_{70}$Ph$_4$, C$_{70}$Ph$_8$, and C$_{70}$Ph$_{10}$, the INDO/SCI calculations (including 5626 configurations) produce a good agreement with the measured absorption spectra over the entire spectral range (even though the convergence of the high lying $S_n\rightarrow S_0$ excitation energies and oscillator strengths is as expected not fully reached for the largest molecules). The high quality of the agreement between the measured and calculated data in the visible region allows the assignment of the spectral features to specific electronic transitions. In particular we show that, for these derivatives, the lowest lying absorption band and the fluorescence band correspond to the first electronic transition $S_1\rightarrow S_0$ (see Table III).

The comparison between the measured and calculated values of the $S_1\rightarrow S_0$ transition suggest that isomer 2 of C$_{70}$Ph$_6$ is responsible for the fluorescence at 728 nm and the lowest absorption band. We note, however, that isomer 2 is not the predicted C$_{70}$Ph$_6$ isomer and moreover that it does not account for all the absorption bands characteristic of C$_{70}$Ph$_6$ in the visible region [Fig. 5(a)]. A reasonable agree-

### Table I. Counting of the bonds on the C$_{70}$ cage according to their single, intermediate or double character (see text for details).

<table>
<thead>
<tr>
<th>C$_{70}$</th>
<th>C$_{70}$Ph$_2$</th>
<th>C$_{70}$Ph$_4$</th>
<th>Isomer 1</th>
<th>Isomer 2</th>
<th>C$_{70}$Ph$_8$</th>
<th>C$<em>{70}$Ph$</em>{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single bonds (C-(sp^3)C)</td>
<td>0</td>
<td>6</td>
<td>12</td>
<td>18</td>
<td>18</td>
<td>24</td>
</tr>
<tr>
<td>Single bonds (C-(sp^3)C)</td>
<td>64</td>
<td>60</td>
<td>52</td>
<td>41</td>
<td>48</td>
<td>43</td>
</tr>
<tr>
<td>Double bonds</td>
<td>20</td>
<td>15</td>
<td>16</td>
<td>14</td>
<td>15</td>
<td>18</td>
</tr>
<tr>
<td>Intermediate bonds</td>
<td>21</td>
<td>24</td>
<td>25</td>
<td>32</td>
<td>24</td>
<td>20</td>
</tr>
</tbody>
</table>

### Table II. Ground-state properties (heat of formation $\Delta H_f$, charge distribution, ionization potential $I$, electron affinity $A$, and HOMO–LUMO gap $\Delta E$) calculated at the AM1 level. The total charge transferred towards the cage and the average contribution of the phenyl groups are given. The INDO/S values for $I$, $A$, and $\Delta E$ are given in parentheses.

<table>
<thead>
<tr>
<th>C$_{70}$</th>
<th>C$_{70}$Ph$_2$</th>
<th>C$_{70}$Ph$_4$</th>
<th>Isomer 1</th>
<th>Isomer 2</th>
<th>C$_{70}$Ph$_8$</th>
<th>C$<em>{70}$Ph$</em>{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H_f$ (kcal mol$^{-1}$)</td>
<td>1061</td>
<td>1111</td>
<td>1112</td>
<td>1152</td>
<td>1145</td>
<td>1156</td>
</tr>
<tr>
<td>Charge distribution (</td>
<td>e</td>
<td>) on C$_{70}$ cage</td>
<td>$-0.088$</td>
<td>$-0.161$</td>
<td>$-0.219$</td>
<td>$-0.228$</td>
</tr>
<tr>
<td>per phenyl on average</td>
<td>$+0.044$</td>
<td>$+0.040$</td>
<td>$+0.037$</td>
<td>$+0.038$</td>
<td>$+0.033$</td>
<td>$+0.029$</td>
</tr>
<tr>
<td>$I$ (eV)</td>
<td>9.14(6.51)</td>
<td>8.45(5.91)</td>
<td>8.80(6.36)</td>
<td>8.11(5.72)</td>
<td>8.51(6.16)</td>
<td>8.74(6.47)</td>
</tr>
<tr>
<td>$A$ (eV)</td>
<td>3.27(1.18)</td>
<td>3.35(1.45)</td>
<td>2.88(1.12)</td>
<td>3.21(1.72)</td>
<td>2.65(1.23)</td>
<td>2.23(0.86)</td>
</tr>
<tr>
<td>$\Delta E$ (eV)</td>
<td>5.87(5.33)</td>
<td>5.10(4.46)</td>
<td>5.92(5.24)</td>
<td>4.90(4.00)</td>
<td>5.86(4.93)</td>
<td>6.51(5.61)</td>
</tr>
</tbody>
</table>
ment between the calculated spectrum of isomer 1 with the experimental data is only obtained when a rigid redshift of about 2000 cm$^{-1}$ for all transitions is adopted. This implies that fluorescence is due to the radiative relaxation from the $S_2$ state and that a low-lying band exists at 1400 nm [Fig. 5(b)]; preliminary experiments in the near-IR region (by using a Perkin-Ellmer spectrophotometer sensitive up to 1100 nm), have failed to prove this hypothesis. Finally, we note that the best agreement between calculated and experimental data is obtained when considering a 50–50 contribution of both isomers to the absorption spectrum [see Fig. 5(c)]; the fluorescence would in that case be that due to isomer 2. The $C_{70}Ph_6$ sample studied is very unlikely, however, to have more than one regioisomer present in view of its characteristic NMR spectra.$^{27}$ It is evident from the above observations that a definitive assignment for the spectral features of $C_{70}Ph_6$ should therefore await new experimental and theoretical investigations.

![Graphical representation of the HOMO and LUMO orbitals on the basis of the INDO/S optimized LCAO coefficients. The participation number PN is given below each orbital representation.](image1)

**FIG. 2.** Graphical representation of the HOMO and LUMO orbitals on the basis of the INDO/S optimized LCAO coefficients. The participation number PN is given below each orbital representation.

![AM1 energies for the HOMO and LUMO orbitals. The dashed lines represent the energy reference for the orbitals of $C_{70}$, from which destabilization effects are measured (double arrows). The calculated value of the HOMO–LUMO gap $\Delta E$ is also shown.](image2)

**FIG. 3.** AM1 energies for the HOMO and LUMO orbitals. The dashed lines represent the energy reference for the orbitals of $C_{70}$, from which destabilization effects are measured (double arrows). The calculated value of the HOMO–LUMO gap $\Delta E$ is also shown.
DISCUSSION

The foregoing bond-length analysis and calculated one-electron properties (ionization potential, electron affinity, spatial localization of HOMO and LUMO) have shown that the geometry and electronic structure are specific for each C_{70}Ph_{2n} derivative studied and that these properties are also very different from those of the parent C_{70} molecule. As expected, the strong perturbation induced by the multifu-
tionalization of the cage has important effects on the photo-
physical properties of these molecules. This is essentially
revealed by the distinctive absorption system each derivative
displays in the visible region, as well as by their fluorescence
spectra. In this discussion, we will focus on the first elec-
tronic transition $S_1 - S_0$.

We have, in first instance, investigated the effect of the
cage conjugation on the energy of the lowest electronic tran-
sition. The results are given in Fig. 6, where the calculated
vertical excitation energies $S_1 - S_0$ for $C_{70}$ and each deriva-
tive are plotted versus the degree of conjugation on the cage
~estimated in a simplified manner from the number of bonds
being of intermediate length between single and double
bonds!. The two quantities correlate well, suggesting, as ex-
pected, that the stronger the conjugation on the cage the
smaller the $S_1 - S_0$ energy separation. For example, $C_{70} \text{Ph}_6$
isomer 1 and $C_{70} \text{Ph}_{10}$, which are the most and the least con-
jugated derivatives, have the lowest and highest $S_1 - S_0$ ver-
tical excitation energies of 1.12 eV and 2.67 eV, respec-
tively. The deviation from a linear relationship that normally
applies for conjugated systems is not surprising if one con-
siders the degree of simplicity of the model. Interestingly,
Fig. 6 shows that the different spectroscopic properties of the
$C_{70} \text{Ph}_n$ isomers (which coincide reasonably well with the se-
quence) can be partly rationalized in terms of conjugation
effects.

The spatial localization of HOMO and LUMO levels,
which is known to influence the energy of these orbitals and
consequently the value of the HOMO–LUMO gap $\Delta E$ (see
for instance Ref. 35), offers an alternative explanation for the
different $S_1 - S_0$ energies reported. The correlation between
the spatial localization (expressed in term of the participation
number PN) and energy of the HOMO and LUMO levels
calculated either at the AM1 or INDO/S level is poorer than
expected (see Fig. 7). The only distinguishable trend that can
be observed from these data is that the energy of the LUMO
level appears to decrease as delocalization on the cage in-
creases (larger value of PN).

It is interesting to compare the photophysical properties
of the $C_{70} \text{Ph}_{2n}$ derivatives investigated, to the results ob-
tained by Schick et al. for the photophysics of two re-
gioisomers ($T_h$ and $D_3$ symmetric) hexapyrrolidino-
derivative of $C_{60}$. These $C_{60}$ derivatives are strongly luminescent, as are the $C_{70} \text{Ph}_{2n}$ derivatives studied in this
work (especially $C_{70} \text{Ph}_8$ and $C_{70} \text{Ph}_{10}$ which show strong eye-
detectable luminescence). Schick et al. have explained the peculiar photophysical behavior of hexapyrrolidine fullerene
derivatives by suggesting that a diminished $\pi$ system on the

<table>
<thead>
<tr>
<th>Table III. Main photophysical properties measured from the absorption and fluorescence spectra. The INDO/SCI value for the vertical excitation energy $S_1 - S_0$ is also given.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{70} \text{Ph}_2$</td>
</tr>
<tr>
<td>---------------------------------------------------------------</td>
</tr>
<tr>
<td>Absorption bands ($\lambda$, nm)</td>
</tr>
<tr>
<td>294</td>
</tr>
<tr>
<td>352</td>
</tr>
<tr>
<td>402</td>
</tr>
<tr>
<td>436</td>
</tr>
<tr>
<td>452</td>
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<tr>
<td>505</td>
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<td>540</td>
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<tr>
<td>576</td>
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<td>620</td>
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<tr>
<td>696</td>
</tr>
<tr>
<td>720</td>
</tr>
<tr>
<td>780</td>
</tr>
<tr>
<td>Fluorescence band ($\lambda$, nm)</td>
</tr>
<tr>
<td>738</td>
</tr>
<tr>
<td>795</td>
</tr>
<tr>
<td>Additional features</td>
</tr>
<tr>
<td>$S_0 - S_1$ excitation energy (eV)</td>
</tr>
<tr>
<td>Calculated</td>
</tr>
<tr>
<td>1.88 (isomer 2)</td>
</tr>
</tbody>
</table>
cage induces a greater energy separation between the \( S_0 \) ground state and both the first excited singlet and triplet states (\( S_1 \) and \( T_1 \)). Thus the radiative rate from \( S_1 \) increases while the rate of radiationless transition from \( T_1 \) decreases. Our results fully corroborate these conclusions about the relationship between the \( S_1 - S_0 \) gap and the degree of conjugation on the cage (Fig. 6). Furthermore, preliminary attempts to characterize the relative fluorescence intensity of the \( C_{70} \) \( Ph_2 \) derivatives with respect to one another also tend to confirm, as suggested by Schick et al., that the fluorescence increases as the cage \( \pi \) system diminishes or accordingly, as the \( S_1 - S_0 \) energy separation increases. In particular, the strongly luminescent \( C_{70} Ph_{10} \) and \( C_{70} Ph_8 \) derivatives are the least conjugated \( C_{70} Ph_{2n} \) derivatives investigated and are characterized by a high-energy first electronic transition. To assess the validity of the present results, the fluorescence quantum yield of each of the \( C_{70} Ph_{2n} \) derivative should, however, be precisely determined.

CONCLUSIONS

We have described the photophysical properties of six multifunctionalized derivatives of \( C_{70} \): \( C_{70} Ph_2 \), \( C_{70} Ph_4 \), \( C_{70} Ph_6 \) (two isomers are considered for the theoretical work), \( C_{70} Ph_8 \), and \( C_{70} Ph_{10} \). The analysis of the absorption and fluorescence spectra of each derivative was based on INDO/
SCI calculations involving 5625 excited configurations. Particular attention was paid to the first electronic transition and to the changes observed in it due to the degree of perturbation of the cage electronic system. We have shown that the cage conjugation simply expressed in terms of geometric arguments plays an important part in influencing the photophysical properties of fullerene derivatives: weaker conjugation induces a blue shift of both the absorption and fluorescence spectra and also produces an increase in fluorescence intensity. These conclusions appear promising for the synthesis of fullerene derivatives with potential applications in optical devices.

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\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{Correlation between the spatial localization of the HOMO and LUMO orbitals on the cage, expressed in term of the participation number PN, and their respective energies. The circles and the crosses give the AM1 and INDO/S calculated energy values, respectively.}
\end{figure}

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