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## Molecular State and Distribution of Fullerenes Entrapped in Sol–Gel Samples<sup>†</sup>

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A novel synthetic method that can encapsulate fullerene molecules (pure C<sub>60</sub>, pure C<sub>70</sub>, or their mixture) over a wide range of concentrations ranging from micromolar to millimolar in hybrid glass by a sol–gel method without any time-consuming, complicated, and unwanted extra steps (e.g., addition of a surfactant or derivatization of the fullerenes) has been successfully developed. The molecular state and distribution of encapsulated fullerene molecules in these sol–gel samples were unequivocally characterized using newly developed multispectral imaging techniques. The high sensitivity (single-pixel resolution) and ability of these instruments to record multispectral images at different spatial resolutions (~10 μm with the macroscopic instrument and ~0.8 μm with the microscopic instrument) make them uniquely suited for this task. Specifically, the imaging instruments can be used to simultaneously measure multispectral images of sol–gel-encapsulated C<sub>60</sub> and C<sub>70</sub> molecules at many different positions within a sol–gel sample in an area either as large as 3 mm × 4 mm (with the macroscopic imaging instrument) or as small as 0.8 μm × 0.8 μm (with the microscopic instrument). The absorption spectrum of the fullerene molecule at each position can then be calculated either by averaging the intensity of a 15 × 15 square of pixels (which corresponds to an area of 3 mm × 4 mm) or from the intensity of a single pixel (i.e., an area of about 0.8 μm × 0.8 μm), respectively. The molecular state and distribution of fullerene molecules within sol–gel samples can then be determined from the calculated spectra. It was found that spectra of encapsulated C<sub>60</sub> and C<sub>70</sub> measured at five different positions within a sol–gel sample were similar not only to one another but also to spectra measured at six different times during the sol–gel reaction process (from *t* = 0 to 10 days). Furthermore, these spectra are similar to the corresponding spectra of monomeric C<sub>60</sub> or C<sub>70</sub> molecules in solution. Similarly, spectra of sol–gel samples containing a mixture of C<sub>60</sub> and C<sub>70</sub> were found to be the same at five different positions, as well as similar to spectra calculated from an average of the spectra of C<sub>60</sub> and C<sub>70</sub> either encapsulated in a sol–gel or in solution. It is evident from these results that C<sub>60</sub> and C<sub>70</sub> molecules do not undergo aggregation upon encapsulation into a sol–gel but rather remain in their monomeric state. Furthermore, entrapped C<sub>60</sub> and C<sub>70</sub> molecules in their monomeric state were distributed homogeneously throughout the entire sol–gel samples. Such a conclusion can be readily, quickly, and easily obtained, not with traditional spectroscopic techniques based on the use of a single-channel detector (absorption, fluorescence, infrared, Raman) but rather with the newly developed multispectral imaging technique. More importantly, the novel synthetic method reported here makes it possible, for the first time, to homogeneously entrap monomeric fullerene molecules (C<sub>60</sub>, C<sub>70</sub>, or their mixture) in a sol–gel at various concentrations ranging from as low as 2.2 mM C<sub>60</sub> (or 190 μM C<sub>70</sub>) to as high as 4.2 mM C<sub>60</sub> (or 360 μM C<sub>70</sub>).

Fullerenes have been the subject of wide and intense study in many disciplines including chemistry, physics, and materials science.<sup>1–4</sup> Because of their unique structure, fullerenes have many interesting and unique properties.<sup>3,4</sup> For example, C<sub>60</sub> molecules are known to exhibit an optical limiting effect.<sup>4</sup> Efforts have been made, therefore, to use C<sub>60</sub> to prepare novel high-performance materials that have this nonlinear optical effect. However, advances in this field are rather limited despite the rather large number of studies. A variety of reasons might account for the lack of success, but one contributing factor is probably the low solubility of fullerenes.<sup>3,4</sup> Specifically, C<sub>60</sub> is known to have a rather low solubility in a variety of solvents, particularly polar solvents. When mixed with other materials, the fullerene molecules tend to undergo self-aggregation, causing undesirable effects including phase separation problems. The

low solubility and poor miscibility lead to poor processibility, which significantly limits the scope of practical applications of fullerenes.

Recent efforts have centered on encapsulating fullerene molecules in sol–gel materials.<sup>5–15</sup> There are several advantages to this approach including the fact that the fullerene molecules are entrapped in the growing network, allowing them to have a high environmental stability. Compared to traditional approaches, the sol–gel method has several advantages including high reactivity, better purity, and operation at relatively lower temperature and mild conditions. The structure of the sol–gel can, therefore, be readily controlled at all stages of the process.<sup>16–22</sup> Unfortunately, despite intense efforts made by various groups, only limited success has been achieved to date.<sup>5–15</sup> Because fullerene has rather low solubility, it often undergoes coagulation during the sol–gel process. As a consequence, the concentration of encapsulated C<sub>60</sub> is often too low for practical use, and the embedded C<sub>60</sub> molecules are not homogeneously distributed in monomeric form throughout the

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glass sample. Various approaches have been applied to ameliorate the low solubility of fullerene. For example, by use of surfactant such as cetyltrimethylammonium bromide (CTAB) to facilitate the dissolution of C<sub>60</sub>, it was possible to prepare sol-gel with embedded C<sub>60</sub>.<sup>14,15</sup> Although effective, this method suffers from complications such as the fact that the added surfactant might modify properties of the glass. In addition, this approach can be used to prepare only thin films of glass, and the encapsulated C<sub>60</sub> molecules are monodisperse in monomeric form only at relatively low concentrations (micromolar).<sup>14,15</sup> Other efforts include functionalizing fullerenes, either with polar groups (amino, hydroxy) or directly with alkoxysilane, to render them better solubility, but they have achieved only limited success.<sup>5-13</sup> Because chemically modified fullerenes can have different properties than the parent fullerenes<sup>6</sup> and because the synthetic schemes involved are complicated and time-consuming and often can be performed only by those with expertise in synthesis, this approach has not been widely used.<sup>5-15</sup> It is thus of particular importance that a novel sol-gel method be developed that is capable of preparing not just thin films but also bulk-size glasses with embedded pure (not functionalized) fullerenes at various concentrations ranging from micromolar to millimolar.

Compounding the aforementioned difficulties is the lack of a suitable spectroscopic method that can determine molecular state (i.e., monomeric or aggregated form) and distribution of doped fullerene molecules over a wide range of concentrations (from micromolar to molar) and simultaneously at many different positions over an entire sol-gel sample. As a consequence, even if fullerenes could be satisfactorily encapsulated in a sol-gel material, it would not be possible to unequivocally characterize them. The multispectral imaging technique described herein offers a solution for this problem.

A multispectral imaging spectrometer is an instrument that can simultaneously record spectral and spatial information about a sample.<sup>23-29</sup> Unlike conventional imaging techniques, which rely on recording a single image using either single- or multiwavelength light for illumination, the multispectral imaging technique records a series of several thousand images, each image at a specific wavelength. That is, it measures absorption spectra of a sample not at a single position, as is the case for conventional spectrophotometers, but simultaneously at many different positions within a sample (by using a focal plan array detector rather than a single-channel detector). Chemical compositions and structures at different positions within a sample can be elucidated from such images.<sup>23-29</sup> The multispectral imaging instrument is particularly suited for the characterization of fullerenes encapsulated in sol-gel samples. Specifically, the imaging instrument can be used to measure spectra of encapsulated fullerene molecules at several different positions within a sol-gel sample simultaneously. The molecular state and distribution of fullerenes encapsulated in a sol-gel sample can then be elucidated from the recorded spectral images. Unfortunately, despite its potential, the multispectral imaging technique has not been used to characterize fullerenes encapsulated in sol-gels. This is due mainly to the lack of a suitable imaging instrument with the required sensitivity and spatial resolution.

We have recently succeeded in developing such a multispectral imaging instrument.<sup>24-29</sup> The high sensitivity and fast scanning ability of this imaging spectrometer enable studies to be performed that, to date, had not been possible using existing techniques. These include the authentication of documents, the determination of chemical inhomogeneities in ethylene/vinyl

acetate copolymers and kinetic inhomogeneities in the curing of epoxy by amine, and the determination of the identities and sequences of peptides synthesized by a combinatorial solid-phase method.<sup>24-29</sup> We also succeeded in improving the spatial resolution of this imaging instrument by coupling it with a microscope.<sup>29</sup> Because of its fast temporal response (milliseconds) and high spatial resolution (approximately micrometers), we were able to use this multispectral imaging microscope to study photoinduced changes of a single unit cell in temperature-sensitive liquid crystals as a function of time and wavelength.<sup>29</sup>

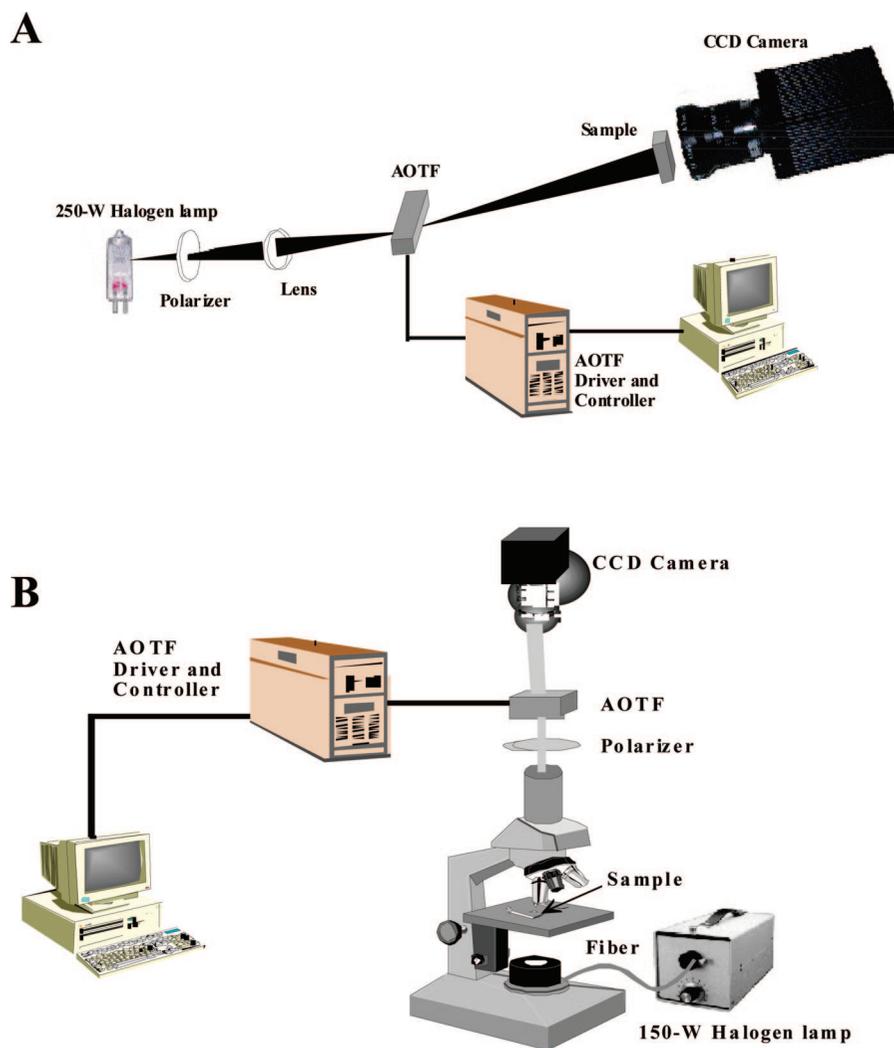
The information presented is indeed provocative and clearly indicates that it is possible to use the multispectral imaging instrument to determine not only the molecular state but also the distribution of fullerene molecules doped in a sol-gel material. Such considerations prompted us to initiate this study, which aims (1) to develop a novel and reproducible synthetic method to encapsulate not only pure C<sub>60</sub> and C<sub>70</sub> but also their mixtures over a wide range of concentrations ranging from micromolar to millimolar in sol-gels without adding any surfactant and (2) to implement the multispectral imaging technique as a sensitive and effective method for characterizing (i.e., determining the molecular state and distribution) encapsulated fullerene molecules within sol-gel materials. Preliminary results on the encapsulation of C<sub>60</sub>, C<sub>70</sub>, and a mixture of the two are reported in this article.

## Experimental Section

**Chemicals and Sol-Gel Preparation.** Phenyltrimethoxysilane, tetraethoxysilane, and hydrochloric acid were obtained from Aldrich Chemical Co.; dichlorobenzene was obtained from Merck; fullerenes [C<sub>60</sub> (99.5%) and C<sub>70</sub> (99%)] were purchased from MER Co., Tucson, AZ; and HEPES buffer was obtained from Sigma Chemicals. All chemicals were used as received.

Because the solubility of the fullerene in silica sol is rather low, a hybrid sol was used. In this case, the hybrid sol contained a mixture of phenyltrimethoxysilane (PTMOS) and tetraethoxysilane (TEOS) in a ratio of 2:1 (v/v). Fullerene was added to the sol as a solution in dichlorobenzene (DCB) (either 10 mg/mL C<sub>60</sub> or 1 mg/mL C<sub>70</sub>). To circumvent problems associated with the low solubility of fullerene in the sol, an appropriate amount of DCB (about 3 mL) was added to the hydrolysis mixture. In fact, it was found that the solubility of the fullerenes in the sol increased as the total volume of DCB added was increased. Hydrochloric acid was used as a catalyst for the hydrolysis of the sol mixture. The amount of water added was found to be dependent on the molar ratio of PTMOS and TEOS; specifically, 1 mol of TEOS requires 4 mol of water, and 1 mol of PTMOS requires 3 mol of water for hydrolysis.

The following protocol was used to prepare sol-gel-encapsulated fullerenes: Reagents were added to a 25 mL-flask in the following order: 2.0 mL of PTMOS, 1.0 mL of TEOS, 3.0 mL of DCB. Fullerene solution in the required concentration (C<sub>60</sub>, C<sub>70</sub>, or a mixture of the two, or pure DCB of the same volume in the case of the blank sol) was then added. Subsequently, 0.1 mL of 0.04 M HCl and 0.5 mL of deionized water were added. For each set of concentrations, four sol-gel samples containing C<sub>60</sub>, C<sub>70</sub>, a mixture of the two, or a blank (without any fullerene) were prepared. They were then sonicated for about 2-3 h in order to obtain a clear silica sol solution. The clear silica sols were then transferred to evaporating disks, and 0.25 mL of 0.25 M HEPES buffer in distilled MeOH (pH 7.5) was added to each sample to adjust the pH to 7.0 to facilitate gelation. The evaporating disks were then placed in a chamber



**Figure 1.** Multispectral imaging instruments for (A) macroscopic and (B) microscopic measurements. AOTF, acousto-optic tunable filter.

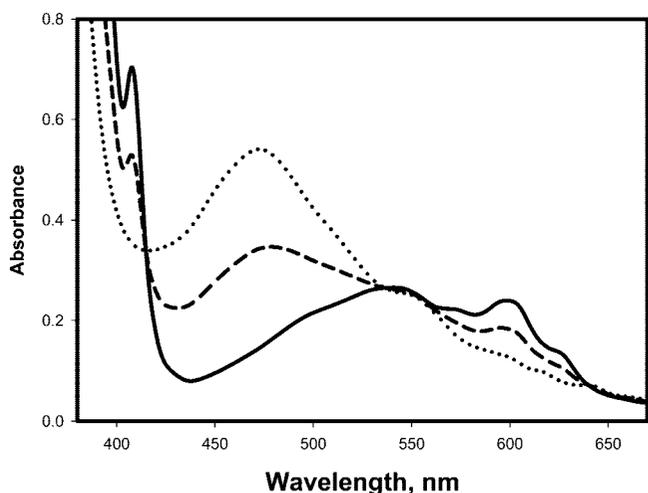
with controlled temperature (25 °C) and humidity (20%). All sols were stirred with a magnetic stirrer for 3–4 h. Fine and dense gels either with or without fullerenes formed within this time. The four gel samples (the blank gel and gels with C<sub>60</sub>, C<sub>70</sub>, and a mixture of the two fullerenes) were then transferred to a homemade 2-mm-path-length cell equipped with four compartments, each of which was 1 cm in width and 2 cm in height. This protocol was found to be effective for the preparation of gels with various thicknesses (from 1 to 5 mm) and with fullerene concentrations as high as 33 mM. At higher concentrations, particularly at 40 mM, fullerenes were found to precipitate in the gel.

It was found that the properties of gels were dependent on their aging conditions, i.e., the conditions under which the remaining solvents were allowed to evaporate. It was found that, when aged in an open evaporating disk, the gels shrank substantially and developed cracks in 2–3 days. In an open four-compartment cell as described above, the gels did not shrink as fast as in an open disk and did not develop any cracks. Gels in the same cells but with aluminum covers did not show any shrinkage in thickness, had no cracks, and became solid in about 10 days.

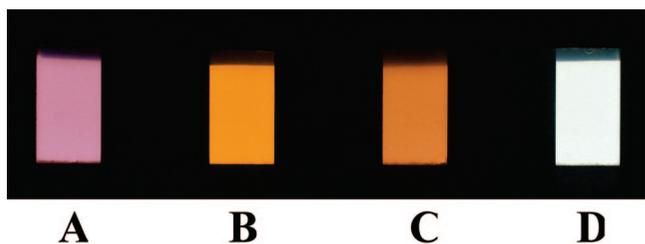
**Instrumentation.** Spectroscopic images were recorded with either a macro- and/or a micromultispectral imaging system. The macroscopic imaging system is similar to the instrument used in our earlier studies for near-infrared imaging,<sup>24–29</sup> except in this case, a CCD UV–visible area camera was used instead

of an NIR focal-plane array camera. A schematic diagram of the macromultispectral imaging instrument is shown in Figure 1A. As illustrated, in this system, a 250-W halogen tungsten lamp was used as the light source. The light was converted into linearly polarized light by means of a polarizer and spectrally dispersed by an acousto-optic tunable filter (AOTF) (Crystal Technology model 97-01776). A home-built radio-frequency driver was used to drive the AOTF to enable it to spectrally tune the incoming light from 400 to 700 nm. The sample was placed in front of the camera and illuminated by the monochromatic light diffracted from the AOTF. Light transmitted from the sample was detected by a 12-bit 1024 × 1024 (12 × 12 μm pixel size) high-frame-rate, progressive-scan silicon area camera (Dalsa model 1M30 CCD camera). A frame grabber (Dipix Corporation model XPG-1000) was used to grab images from the camera for subsequent transfer to the computer for imaging processing.

The spectroscopic imaging system described above was coupled with a Leitz microscope (with minor optical modifications) to facilitate microscopic imaging. As shown in Figure 1B, in this microscopic system, the sample, placed on a microscope stage, was illuminated by light from a 150-W halogen tungsten lamp through a fiber. Light transmitted from the sample and through the microscope lens and a polarizer was then spectrally dispersed by the AOTF before being detected by the Dalsa area camera.



**Figure 2.** Absorption spectra of solutions of  $C_{60}$  (1.0 mg/mL) (—),  $C_{70}$  (0.1 mg/mL) (· · ·), and their mixture at one-half concentration each (— —).



**Figure 3.** Images of sol-gel samples doped with (A)  $C_{60}$ , (B)  $C_{70}$ , (C) their mixture at one-half concentration each, and (D) blank (without any doping).

## Results and Discussion

Absorption spectra of dichlorobenzene solutions of  $C_{60}$  (1.0 mg/mL) and  $C_{70}$  (0.1 mg/mL) are shown as solid and pointed lines, respectively, in Figure 2. As illustrated, the spectrum of  $C_{60}$  solution is rather broad and contains several overlapping bands with maxima at about 400, 545, 600, and 621 nm.  $C_{70}$  also absorbs in this region, but its absorption maximum is shifted toward shorter wavelength (470 nm). As expected, these spectra agree well with those in the literature,<sup>14,15,30–32</sup> and the presence of these bands, particularly the 400-, 600-, and 621-nm bands of  $C_{60}$ , is a clear indication that the  $C_{60}$  and  $C_{70}$  molecules are in monomeric form.<sup>14,15</sup> Also shown in the figure is the spectrum of a solution containing a mixture of these two fullerenes at one-half concentration each (0.5 mg/mL  $C_{60}$  and 0.05 mg/mL  $C_{70}$ ). This spectrum is, as expected, an average of the spectra of  $C_{60}$  and  $C_{70}$ .

Shown in Figure 3 are pictures of sol-gel samples without and with  $C_{60}$ ,  $C_{70}$ , or their mixture. As expected, the sol-gel undergoes color changes when doped with fullerenes. This is due to the inherent colors of  $C_{60}$ ,  $C_{70}$ , and their mixture. However, it seems that the optical quality of the sol-gel glass remains the same. These results seem to suggest that  $C_{60}$  and  $C_{70}$  molecules do not undergo self-aggregation but rather distribute homogeneously within the sol-gel samples. Additional support for this possibility and detailed information on the molecular state and distribution of the encapsulated fullerene molecules, deduced from the results of the micro- and macroscopic multispectral imaging measurements, are presented in the following sections.

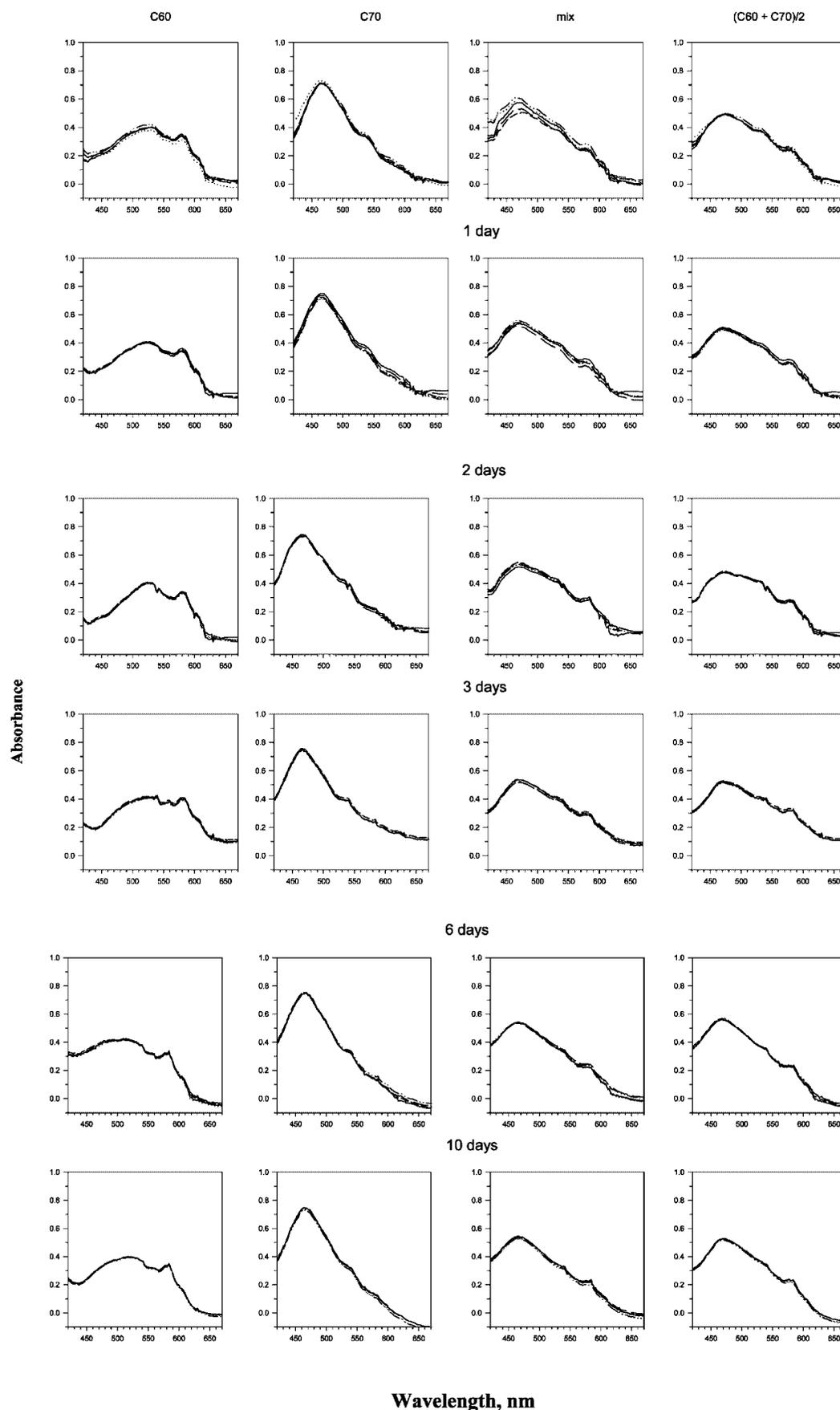
**Macroscopic Multispectral Imaging Measurements.** As described in the Experimental Section, for each experiment, a

set of four sol-gel samples were prepared: a blank sol-gel and sol-gels doped with  $C_{60}$ ,  $C_{70}$ , and a mixture of the two (at one-half concentration each). These four samples were placed into a four-compartment, 2-mm-path-length cell for measurements. Images of each of these four samples were recorded by the CCD camera from 425 to 675 nm at 2-nm intervals (by scanning the AOTF). Absorption spectra at various locations within a sample were obtained by comparing the intensity of the corresponding pixel (or an average of pixels) in each image. The first column of Figure 4 shows six sets of spectra of a sol-gel sample doped with 3.30 mM  $C_{60}$  taken at various times during the sol-gel reaction process [ $t = 0$  (on preparation), 1, 2, 3, 6, and 10 days] using the macromultispectral imaging instrument shown in Figure 1A. At each reaction time, there are five spectra in each set, which were recorded at five different positions within a sol-gel sample. Each spectrum was obtained by taking an average of the intensity of a  $15 \times 15$  square of pixels. The same five positions were used to calculate five sets of spectra for the sample at six different reaction times. As illustrated, at the beginning of the sol-gel process, there were small differences among the spectra of  $C_{60}$  at different positions within the sol-gel sample. However, these differences were relatively small and disappeared as the reaction proceeded. There were no differences among the spectra after 1 day. Furthermore, upon comparison of the six sets of spectra (at different times), it is evident that the spectra of the encapsulated  $C_{60}$  are similar not only at different positions within a sol-gel sample but also at different reaction times. Additionally, the spectra of the encapsulated  $C_{60}$  presented here are very similar to that of monomeric  $C_{60}$  in dichlorobenzene solution (Figure 2). Taken together, these results indicate not only that the  $C_{60}$  molecules did not undergo self-aggregation upon encapsulation but also that they were distributed homogeneously within the sol-gel sample.

The spatial resolution of the macromultispectral imaging instrument (Figure 1A) was determined to be  $\sim 10 \mu\text{m}/\text{pixel}$ . Because the CCD camera is equipped with  $1024 \times 1024$  pixels, this corresponds to a recording an area of  $10 \text{ mm} \times 10 \text{ mm}$  of a sample. The five positions from which data were used to calculate spectra were from  $X/Y$  pixel positions of 300/500, 300/800, 500/650, 670/570, and 700/800. These positions correspond to an area approximately 3 mm in width and 4 mm in height. It is, therefore, not unreasonable to suggest that the encapsulated  $C_{60}$  molecules distributed homogeneously throughout the sol-gel samples.

Images of a sol-gel sample doped with 280  $\mu\text{M}$   $C_{70}$  (in the second compartment of the four-compartment cell) were also recorded at six different times of the sol-gel reaction process ( $t = 0, 1, 2, 3, 6,$  and  $10$  days), and the results are shown in the second column of Figure 4. As for the case of the sol-gel-encapsulated  $C_{60}$ , the spectra of the encapsulated  $C_{70}$  are similar not only at five different positions within a sol-gel sample but also at different reaction times. Furthermore, the spectra of the encapsulated  $C_{70}$  are similar to the spectrum of monomeric  $C_{70}$  in dichlorobenzene solution (Figure 2). These results seem to suggest that, similarly to encapsulated  $C_{60}$ , the  $C_{70}$  molecules did not undergo self-aggregation upon encapsulation and were distributed homogeneously within the sol-gel sample.

The third column of Figure 4 shows results obtained from a sol-gel sample doped with a mixture of  $C_{60}$  and  $C_{70}$  (1.65 mM  $C_{60}$  and 140  $\mu\text{M}$   $C_{70}$ ). As illustrated, the fullerene mixture exhibits similar absorption spectra at five different positions within the sample at all six recording times. The results suggest that the  $C_{60}$  and  $C_{70}$  were distributed homogeneously throughout



**Figure 4.** Spectra of sol-gel samples doped with 3.30 mM C<sub>60</sub> (first column), 280  $\mu$ M C<sub>70</sub> (second column), and their mixture at one-half concentration each (third column) and spectra calculated from the spectra of the first and third columns (fourth column). These spectra were calculated from the multispectral images recorded using the macroscopic imaging instrument shown in Figure 1A. For each sample, six sets of spectra were obtained at six different reaction times ( $t = 0, 1, 2, 3, 6,$  and  $10$  days). At each reaction time, there are five spectra in each set, which were recorded at five different positions within a sol-gel sample. Each spectrum was obtained by taking an average of the intensity of a  $15 \times 15$  square of pixels.

the sample. Information on the molecular states of  $C_{60}$  and  $C_{70}$  can be deduced by comparing the spectra presented in this column with those in the fourth column [labeled as  $(C_{60} + C_{70})/2$ ], which were obtained by taking the averages of the corresponding spectra in the first and second columns for sol-gel samples doped with either  $C_{60}$  or  $C_{70}$ , separately. It is possible to perform this comparison because the concentrations of  $C_{60}$  and  $C_{70}$  in the mixture are 1.65 mM and 140  $\mu\text{M}$ , which are one-half of the concentrations of  $C_{60}$  and  $C_{70}$  in the sol-gel samples encapsulated with only one fullerene (i.e., the sol-gel samples shown in the first and second columns were doped with either 3.30 mM  $C_{60}$  or 280  $\mu\text{M}$   $C_{70}$ ). Because it was found that  $C_{60}$  and  $C_{70}$  molecules did not undergo self-aggregation when they were individually encapsulated into the sol-gel samples, any difference between the spectra of the mixture (third column) and the calculated spectra (fourth column) is an indication of changes in the molecular states of the  $C_{60}$  and  $C_{70}$  when they were doped as a mixture. As illustrated, the spectra of the mixture shown in the third column are very similar to the corresponding calculated spectra shown in the fourth column. The observed similarity clearly indicates that the  $C_{60}$  and  $C_{70}$  molecules in the mixture in this sol-gel sample did not undergo any self-aggregation.

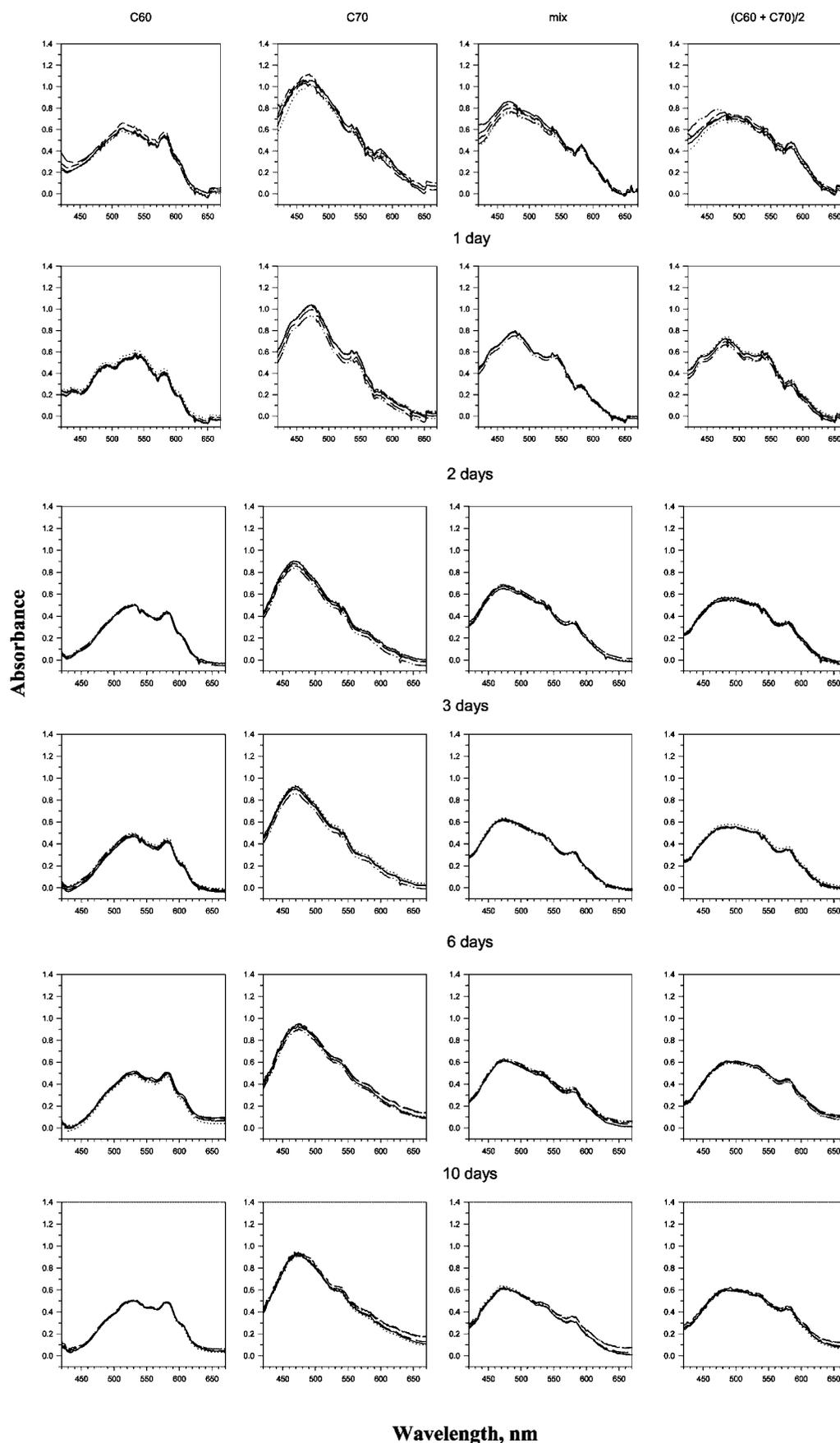
Taken together, the results presented clearly demonstrate that, when doped in the sol-gel samples either as individual components or as a mixture,  $C_{60}$  and  $C_{70}$  molecules do not undergo any self-aggregation and are distributed homogeneously throughout the samples. Because the molecular states and distributions of the doped fullerenes can be affected by their concentrations, it is important to verify that this conclusion is not specific for these concentrations (3.3 mM  $C_{60}$ , 280  $\mu\text{M}$   $C_{70}$ , and their mixture at one-half concentration each) but rather is valid for other concentrations as well. Accordingly, experiments were performed with sol-gel doped with  $C_{60}$ ,  $C_{70}$ , and their mixture at concentrations higher and lower than those used above. Shown in Figure 5 are results for sol-gel doped with 4.2 mM  $C_{60}$ , 360  $\mu\text{M}$   $C_{70}$ , or their mixture at one-half concentration each. These concentrations are about 27% higher than the concentrations used previously for Figure 4. As illustrated, even at these high concentrations, spectra of the encapsulated fullerenes, either as individual components or as a mixture, are not only similar at five different positions for any given times but also are similar at six different reaction times. The same observation was also found when the concentrations of doped fullerenes were reduced by 33% to 2.2 mM  $C_{60}$ , 190  $\mu\text{M}$   $C_{70}$ , and their mixture at one-half concentration each (Figure 6). It is evident that the molecular states and distributions of the fullerenes remain the same when they were encapsulated in sol-gel samples at concentrations as high as 4.2 mM  $C_{60}$  (or 360  $\mu\text{M}$   $C_{70}$ ) or as low as 2.2 mM  $C_{60}$  (or 190  $\mu\text{M}$   $C_{70}$ ). Collectively, the results presented suggest that, in the concentration range used in this study (2.2–4.2 mM for  $C_{60}$  and 190–369  $\mu\text{M}$  for  $C_{70}$ ),  $C_{60}$  and  $C_{70}$  molecules do not undergo any aggregation when they are encapsulated and are distributed homogeneously throughout the sol-gel samples regardless of whether they are doped as individual components or as a mixture. This conclusion was derived from the results obtained using the macroscopic multispectral imaging instrument shown in Figure 1A. This instrument has a spatial resolution of about 10  $\mu\text{m}$ . It would be of particular interest to know whether this conclusion is still valid at much smaller dimensions, e.g.,  $\sim 1$   $\mu\text{m}$ . As described in the following section, a multispectral imaging microscope (shown in Figure 1B) that has a spatial

resolution of about 0.8  $\mu\text{m}/\text{pixel}$  was used to find the answer to this question.

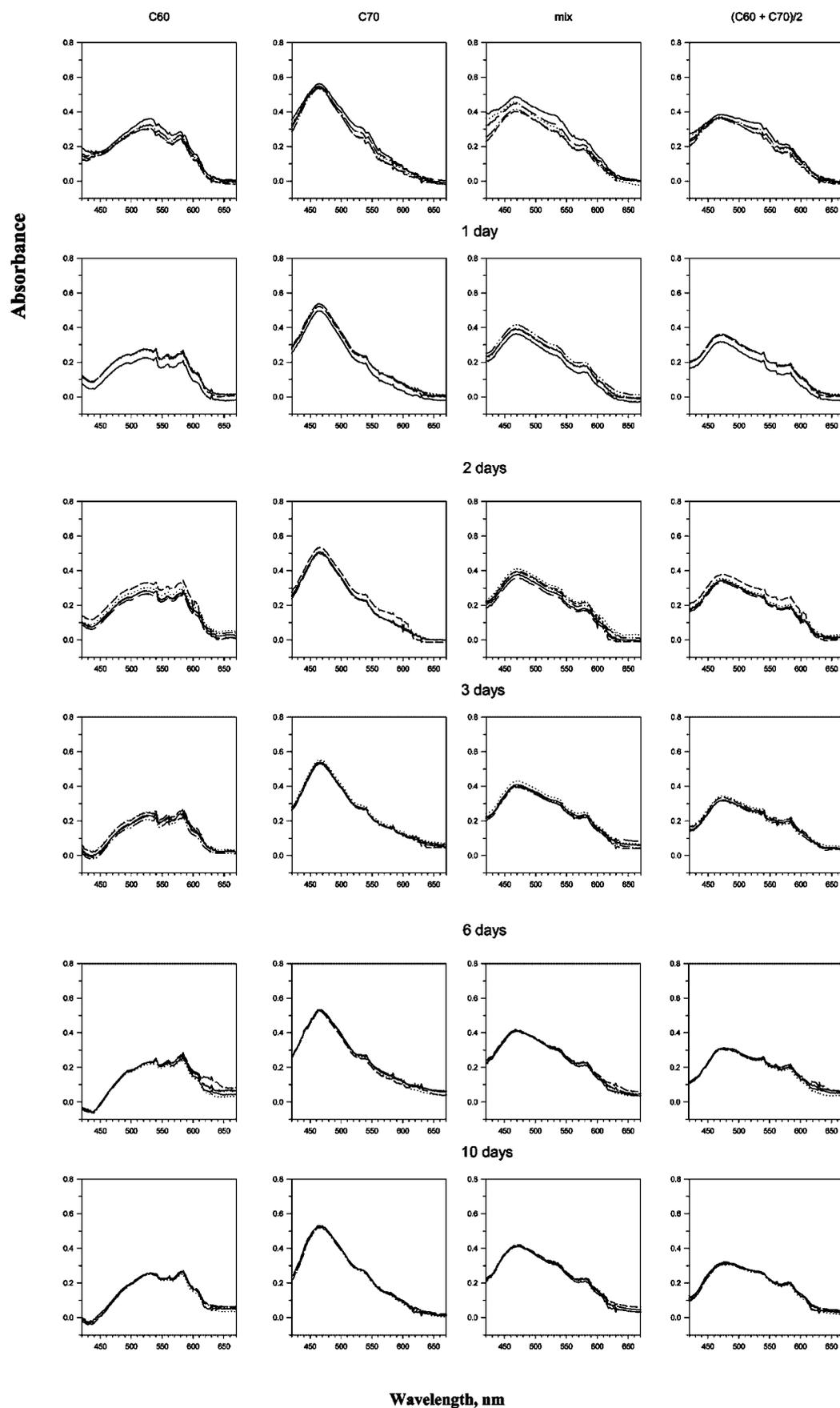
**Microscopic Multispectral Imaging Measurements.** Figure 7 shows spectra of sol-gel samples doped with 3.3 mM  $C_{60}$  (first column), 280  $\mu\text{M}$   $C_{70}$  (second column), and their mixture at one-half concentration each (third column). These spectra were obtained by using the microscopic multispectral imaging instrument shown in Figure 1B to record spectral images of the samples. As for the microscopic measurements shown in Figures 4–6, six sets of spectra were recorded at six different reaction times ( $t = 0, 1, 2, 3, 6,$  and  $10$  days). At each reaction time, there are five spectra for each set, and each spectrum of a set was calculated, not from an average of a  $15 \times 15$  square of pixels as in the macroscopic measurements described above, but rather from a single pixel at five different positions within a sol-gel sample. It is evident from the figure that, as the sol-gel reaction proceeded, some minor changes in the spectra of the doped fullerenes occurred (see, for example, spectra at time  $t = 0$  and those at  $t = 10$  days). However, at any given reaction time, the spectra of doped fullerenes,  $C_{60}$ ,  $C_{70}$ , and their mixture, at five different positions of a sol-gel sample are very similar. Additionally, the spectra of the sol-gel doped with a mixture of  $C_{60}$  and  $C_{70}$  (third column) are very similar to the spectra calculated from one-half of the sum of the spectra of the individually doped samples. Because the concentrations of doped fullerenes in these samples are the same as those used for the macroscopic measurements (Figure 4), the results presented here together with those in the previous section suggest that fullerene molecules do not aggregate upon encapsulation in the sol-gel and that they are distributed homogeneously throughout the sample on a microscopic scale ( $\sim 10$   $\mu\text{m}$ ) as well as on a microscopic scale of about 0.8  $\mu\text{m}$ . It is important to add that this conclusion is valid not only for sol-gel samples doped with  $C_{60}$ ,  $C_{70}$ , and their mixture at the concentrations listed here (i.e., Figures 4 and 7 for 3.3 mM  $C_{60}$ , 280  $\mu\text{M}$   $C_{70}$ , and their mixture at one-half concentration each) but also for samples doped with relatively lower and higher concentrations of  $C_{60}$  and  $C_{70}$ . Specifically, Figure 8 shows spectra for sol-gel samples doped with relatively higher concentrations [4.2 mM  $C_{60}$  (first column), 360  $\mu\text{M}$   $C_{70}$  (second column), and their mixture at one-half concentration each (third column)]. It is evident from the figure that, at any given reaction time, the spectra of doped fullerenes,  $C_{60}$ ,  $C_{70}$ , and their mixture, at five different positions of a sol-gel sample are very similar. Additionally, the spectra of a sol-gel sample doped with a mixture of  $C_{60}$  and  $C_{70}$  (third column) are very similar to the spectra calculated from one-half of the sum of the spectra of the individually doped samples (fourth column). Similar observations can also be made for samples doped with relatively lower concentrations of fullerenes [Figure 9 for 2.2 mM  $C_{60}$  (first column), 190  $\mu\text{M}$   $C_{70}$  (second column), and their mixture at one-half concentration each (third column)].

## Conclusions

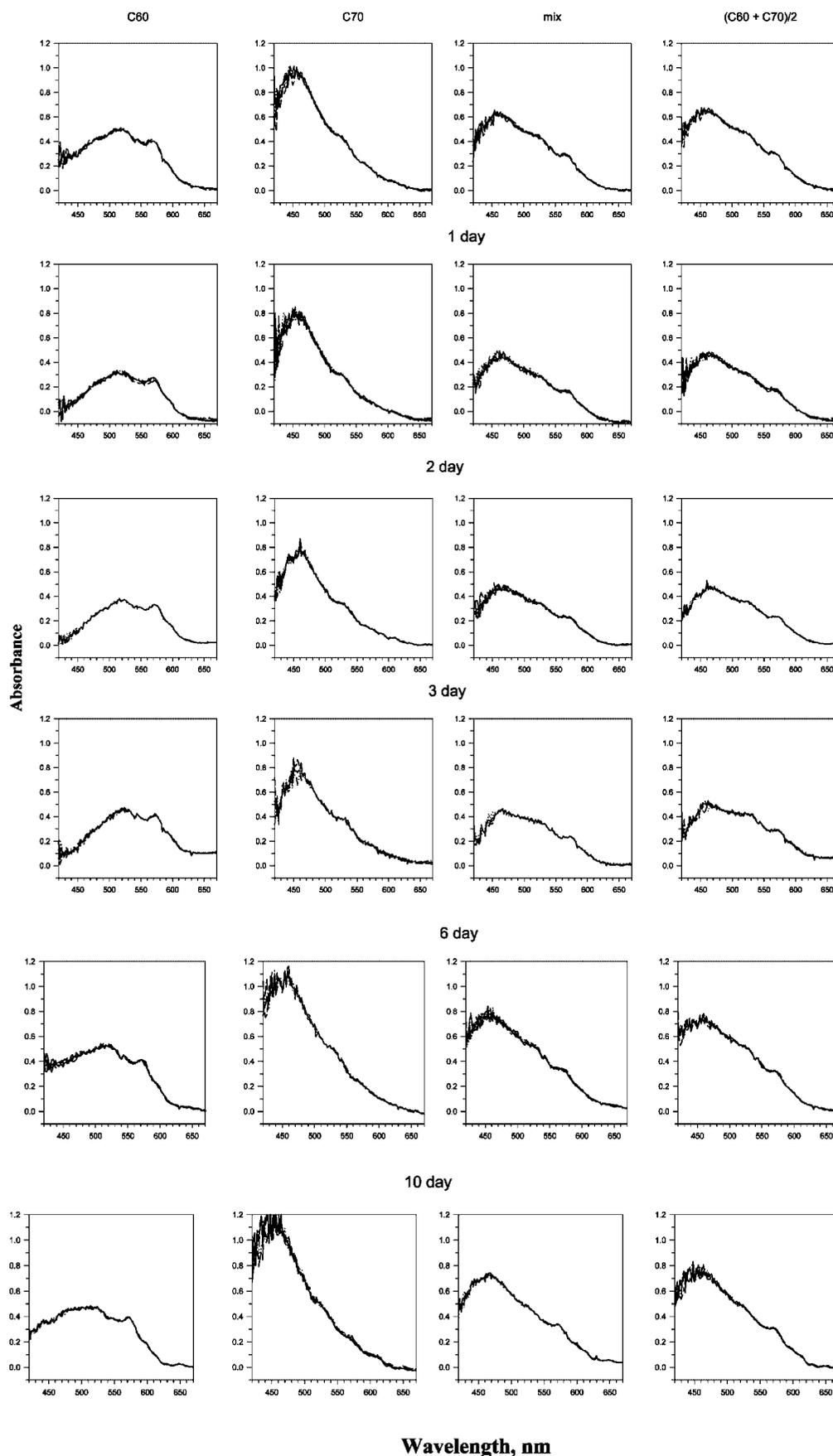
In summary, we have successfully demonstrated the development of (1) a novel and effective synthetic method for preparing sol-gel materials that can entrap different types of fullerenes including  $C_{60}$  and  $C_{70}$  either by themselves or as a mixture and (2) novel techniques for characterizing the molecular state and distribution of the encapsulated fullerenes. The synthetic method reported here makes it possible, for the first time, to encapsulate fullerene molecules (pure  $C_{60}$ , pure  $C_{70}$ , and their mixture) over a wide range of concentrations ranging from micromolar to millimolar, in hybrid glass by a sol-gel method without any



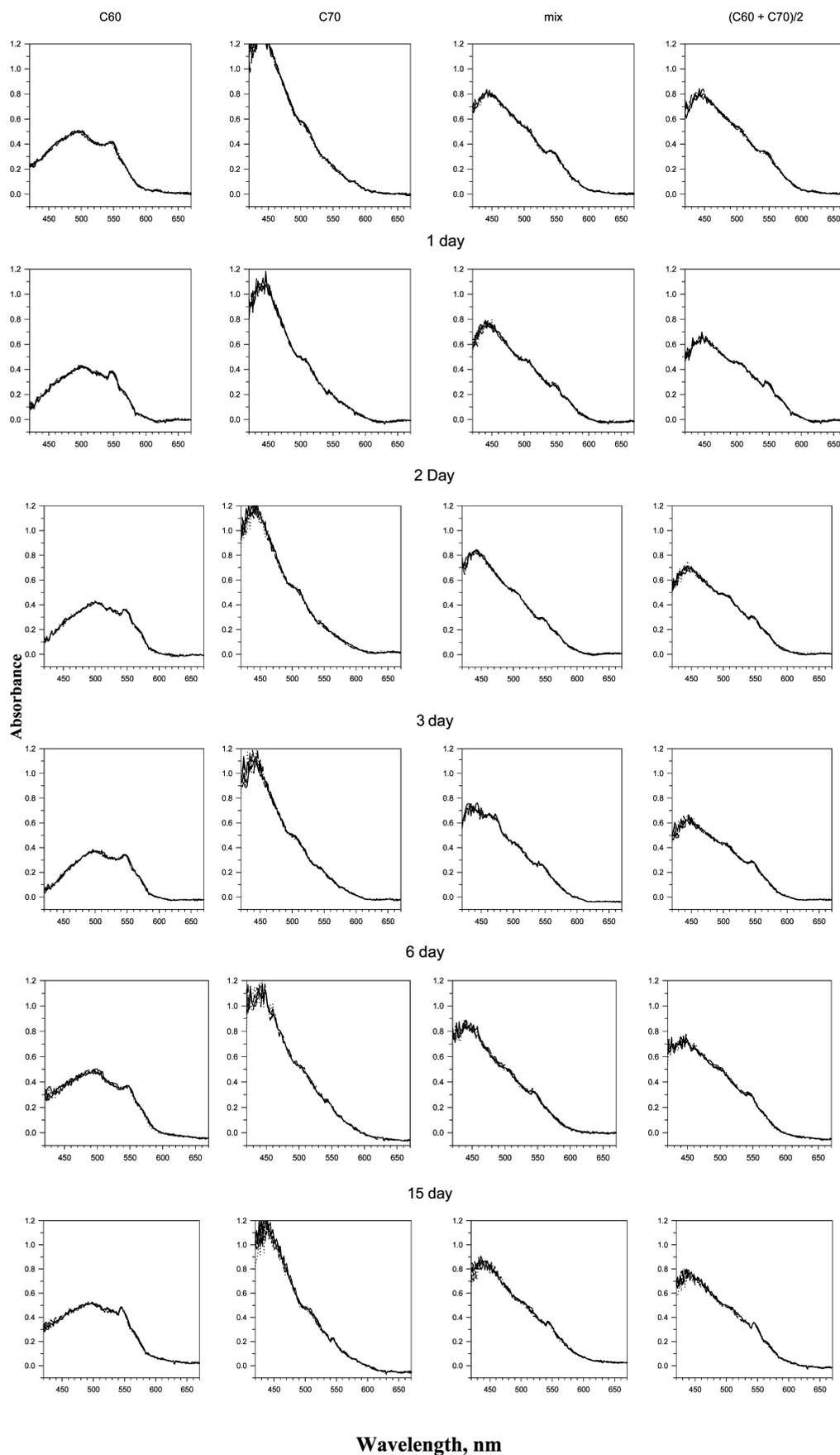
**Figure 5.** Spectra of sol-gel samples doped with 4.20 mM  $C_{60}$  (first column), 360  $\mu\text{M}$   $C_{70}$  (second column), or their mixture at one-half concentration each (third column). (The fourth column shows spectra calculated from the spectra of the first and third columns.) As for the spectra shown in Figure 4, these spectra were calculated from spectral images recorded with the macroscopic imaging instrument (Figure 1A). Six sets of spectra were recorded at six different reaction times, with each set containing five spectra corresponding to five different positions within a sample.



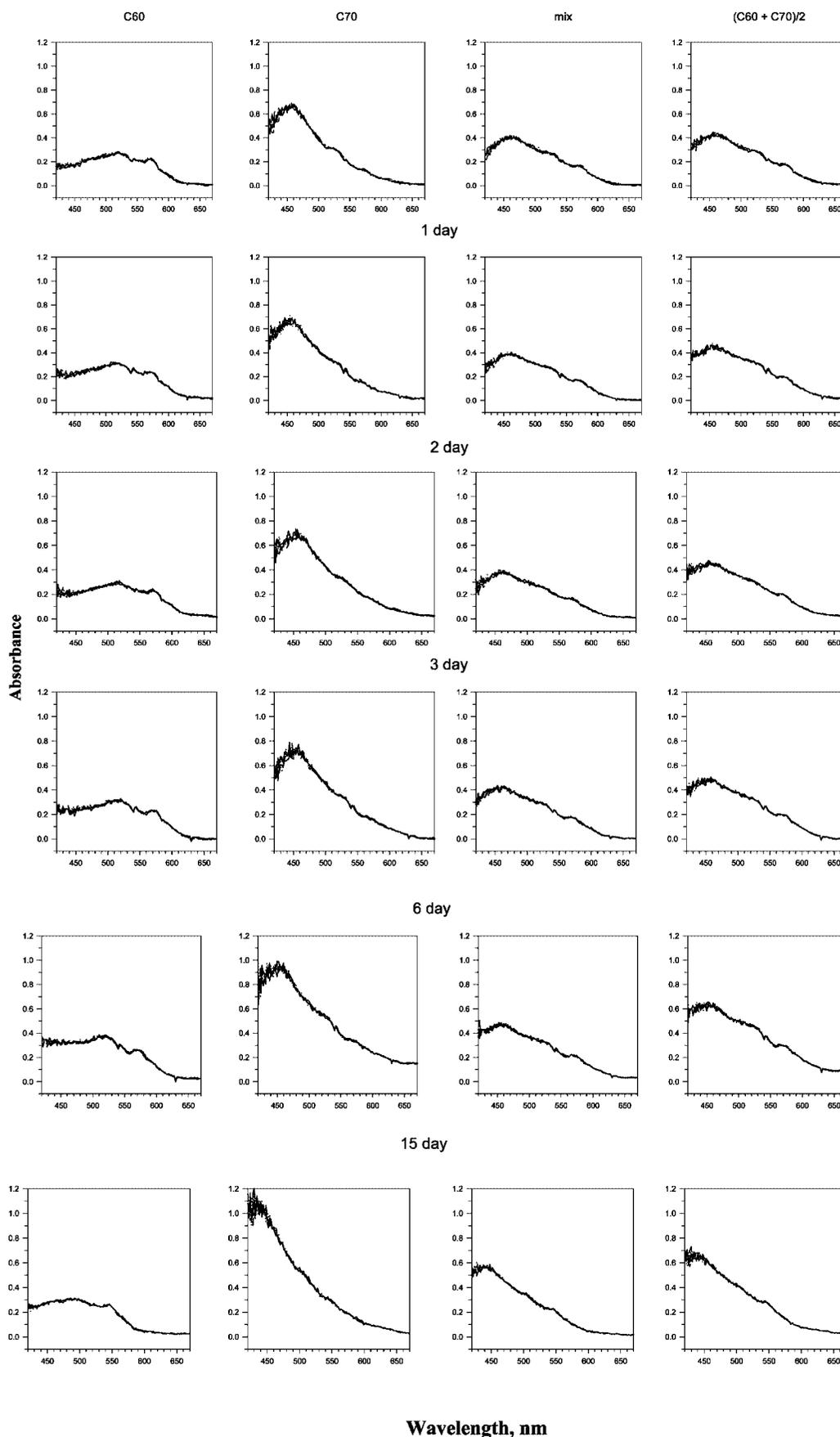
**Figure 6.** Spectra of sol-gel samples doped with 2.20 mM C<sub>60</sub> (first column), 190  $\mu$ M C<sub>70</sub> (second column), or their mixture at one-half concentration each (third column). (The fourth column shows spectra calculated from the spectra of the first and third columns.) As for the spectra shown in Figure 4, these spectra were calculated from spectral images recorded with the macroscopic imaging instrument (Figure 1A). Six sets of spectra were recorded at six different reaction times, with each set containing five spectra corresponding to five different positions within a sample.



**Figure 7.** Spectra of sol-gel samples doped with 3.30 mM  $C_{60}$  (first column), 280  $\mu\text{M}$   $C_{70}$  (second column), and their mixture at one-half concentration each (third column) and spectra calculated from the spectra of the first and third columns (fourth column). These spectra were calculated from the multispectral images recorded using the microscopic imaging instrument shown in Figure 1B. For each sample, six sets of spectra were recorded at six different reaction times ( $t = 0, 1, 2, 3, 6,$  and  $10$  days). At each reaction time, there are five spectra in each set. Each spectrum of a set was calculated from a single pixel at one of five different positions within a sol-gel sample.



**Figure 8.** Spectra of sol-gel samples doped with 4.20 mM  $C_{60}$  (first column), 360  $\mu\text{M}$   $C_{70}$  (second column), or their mixture at one-half concentration each (third column). (The fourth column shows spectra calculated from the spectra of the first and third columns.) As for the spectra shown in Figure 7, these spectra were calculated from spectral images recorded with the microscopic imaging instrument (Figure 1B). Six sets of spectra were recorded at six different reaction times, and each spectrum of a set was calculated from a single pixel at one of five different positions within a sol-gel sample.



**Figure 9.** Spectra of sol-gel samples doped with 2.20 mM  $C_{60}$  (first column), 190  $\mu\text{M}$   $C_{70}$  (second column), or their mixture at one-half concentration each (third column). (The fourth column shows spectra calculated from the spectra of the first and third columns.) As for the spectra shown in Figure 7, these spectra were calculated from spectral images recorded with the microscopic imaging instrument (Figure 1B). Six sets of spectra were recorded at six different reaction times, and each spectrum of a set was calculated from a single pixel at one of five different positions within a sol-gel sample.

time-consuming, complicating, and unwanted extra steps such as addition of a surfactant or derivatization of fullerenes.

Encapsulated fullerene molecules were successfully characterized by use of the recently developed multispectral imaging technique. Because the multispectral imaging instruments have high sensitivity (single-pixel resolution) and can record spectroscopic images at different spatial resolutions ( $\sim 10 \mu\text{m}$  with the macroscopic instrument and  $\sim 0.8 \mu\text{m}$  with the microscopic instrument), they are particularly well suited for this task. Specifically, these imaging instruments were used to simultaneously measure absorption spectra of sol-gel-encapsulated  $\text{C}_{60}$  and  $\text{C}_{70}$  molecules at many different positions within a sol-gel sample. By using either the macroscopic instrument or the microscopic instrument, a spectrum at each position can be calculated from the average intensity of a  $15 \times 15$  square of pixels (in this case, each pixel corresponds to  $10 \mu\text{m} \times 10 \mu\text{m}$ , and the area defined by the five positions is as large as  $3 \text{ mm} \times 4 \text{ mm}$ ) or from the intensity of a single pixel (i.e., an area about  $0.8 \mu\text{m} \times 0.8 \mu\text{m}$ ), respectively. Not only were the spectra of encapsulated  $\text{C}_{60}$  and  $\text{C}_{70}$  measured at five different positions within a sol-gel sample similar to each other, but they were also similar to the corresponding spectra of monomeric  $\text{C}_{60}$  and  $\text{C}_{70}$  in solution. Similarly, spectra of sol-gel samples containing mixtures of  $\text{C}_{60}$  and  $\text{C}_{70}$  were found to be the same at five different positions and to be similar to spectra calculated from the average of spectra of  $\text{C}_{60}$  and  $\text{C}_{70}$  either encapsulated in a sol-gel or in solution. It is evident from these results that  $\text{C}_{60}$  and  $\text{C}_{70}$  molecules do not undergo aggregation upon encapsulation into sol-gel materials but rather remain in their monomeric state. Entrapped  $\text{C}_{60}$  and  $\text{C}_{70}$  molecules in their monomeric state were distributed homogeneously throughout the sol-gel samples. The fact that the spectra of entrapped fullerenes were the same regardless of whether they were calculated from an area as large as  $3 \text{ mm} \times 4 \text{ mm}$  or an area as small as  $0.8 \mu\text{m} \times 0.8 \mu\text{m}$  indicates that the homogeneous distribution of monomeric fullerene molecules was not localized and/or particular to any specific position or area but rather applied to the entire sol-gel sample. Such a conclusion can be readily, quickly, and easily obtained with the newly developed multispectral imaging technique reported here, but not with traditional spectroscopic techniques based on the use of single-channel detection (absorption, fluorescence, infrared, and Raman). More importantly, the novel synthetic method reported here makes it possible, for the first time, to homogeneously entrap monomeric fullerene molecules ( $\text{C}_{60}$ ,  $\text{C}_{70}$ , and their mixture) in sol-gel samples at various concentrations ranging from as low as  $2.2 \text{ mM}$   $\text{C}_{60}$  (or  $190 \mu\text{M}$   $\text{C}_{70}$ ) to as high as  $4.2 \text{ mM}$   $\text{C}_{60}$  (or  $360 \mu\text{M}$   $\text{C}_{70}$ ). To our knowledge, this is the first time that fullerene-encapsulated sol-gel materials with such high concentrations and superior optical and chemical properties have been prepared. It is expected that such sol-gel materials would have desirable properties including nonlinear optical properties. These possibilities are the subject of our current investigations.

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