Chem. Mater. **2003,** *15,* 4739−4744

Nanoscale Cavities for Fulleropyrrolidinium in Nafion Membrane

Junxin Li,[†,‡,§] Shuang Zhang,[†,‡] Pu Zhang,[†,‡] Dongfang Liu,[†] Zhi-Xin Guo,*[,†]
Cheng Ye,[†] and Daoben Zhu[†]

Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China, Graduate School of Chinese Academy of Sciences, Beijing 100080, China, and College of Sciences, Hebei University of Science and Technology, Shijiazhuang 050018, China

Received June 16, 2003. Revised Manuscript Received October 1, 2003

A general method was developed to incorporate fulleropyrrolidinium into the nanoscale cavities of Nafion membrane through electrostatic interaction. The aggregated sizes and structures of fulleropyrrolidinium were controlled by the cavities of Nafion membrane, which were confirmed by XPS and TEM studies. The incorporation was a diffusion-controlled process as evidenced from the absorption spectroscopic method. The absorption spectra of fulleropyrrolidinium nanoaggregates extended to the near-IR region and the fluorescence emission spectra were red-shifted due to the formation of excimers. The resulting fulleropyrrolidinium−Nafion nanocomposites exhibit significant optical-limiting effects at both 532 and 1064 nm, which imply their potential as broadband optical limiters to protect optical devices from damage by lasers.

Introduction

Nafion membranes are perfluorosulfonate ionomers composed of perfluoroethylene chains with pendant sulfonate groups. It has been proposed that the Nafion membranes possess network structures with interconnected reverse micelle-like ion clusters, as schematically shown in Figure 1.[1−2] While Nafion films have been used extensively for applications in modern battery, fuel cell, and sensor technologies,[3,4] their well-defined microstructures, together with their exceptional optical, chemical, thermal, and mechanical properties, have also made Nafion films ideal templates for the preparation of nanoscale particles.[5−16] For example, nanoscale CdS and CdSe could be formed in Nafion membrane by coexchanging Cd^{2+} with an inert diluent ion of Ca^{2+} in the Nafion film followed by dehydration and reaction with H_2S or H_2Se.[10] Other nanoscale inorganic particles such as Ag_2S,[14] Ag,[14] and nanocrystalline TiO_2[15] could also be prepared in Nafion membrane in a similar manner.

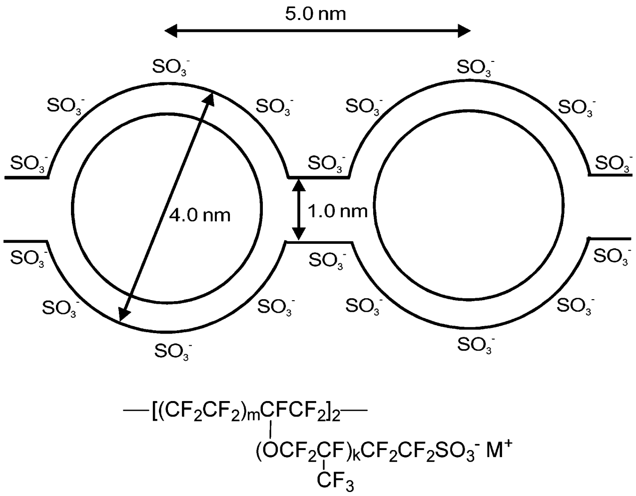


Figure 1. Ion cluster model proposed for the Nafion membrane in the literature.[2]

Recently, we[16] reported the fabrication of the first fullerene-incorporated Nafion membrane. A novel methanofullerene derivative (TDC_{60}, Scheme 1) with inner hydrophobic chains and peripheral hydrophilic chains

---

* Corresponding author. Tel: 86-10-62567034. Fax: 86-10-62559373. E-mail: gzhixin@iccas.ac.cn.

[†] Institute of Chemistry, Chinese Academy of Sciences.

[‡] Graduate School of Chinese Academy of Sciences.

[§] Hebei University of Science and Technology.

(1) Hsu, W. Y.; Gierker, T. D. *J. Membr. Sci.* **1983**, *13*, 307.

(2) *Perfluorinated Ionomer Membranes*; Eisenberg, A., Yeager, H. L., Eds.; American Chemical Society: Washington, DC, 1982.

(3) Heitner-Wirguin, C. *J. Membr. Sci.* **1996**, *120*, 1.

(4) Wang, J.; Musameh, M.; Lin, Y. *J. Am. Chem. Soc.* **2003**, *125* (9), 2408.

(5) Krishnan, M.; White, J. R.; Fox, M. A.; Bard, A. J. *J. Am. Chem. Soc.* **1983**, *105*, 7002.

(6) Wang, Y.; Mahler, W. *Opt. Commun.* **1987**, *61*, 233.

(7) Hilinski, E. F.; Lucas, P. A.; Wang, Y. *J. Chem. Phys.* **1988**, *89*, 3435.

(8) Wang, Y.; Suna, A.; McHugh, J.; Hilinski, E. F.; Lucas, P. A.; Johnson, R. D. *J. Phys. Chem.* **1990**, *92*, 6927.

(9) Smotkin, E. S.; Brown, R. M.; Radenburg, L. K.; Salomon, K.; Bard, A. J.; Campion, A.; Fox, M. A.; Mallouk, T. E.; Webber, S. E.; White, J. M. *J. Fluorine Chem.* **1990**, *94*, 7543.

(10) Smotkin, E. S.; Brown, R. M.; Rabenberg, L. K.; Salomon, K.; Bard, A. J.; Campion, A.; Fox, M. A.; Mallouk, T. E.; Webber, S. E.; White, J. M. *J. Phys. Chem.* **1990**, *94*, 7543.

(11) Zen, J.-M.; Chen, G.; Fan, F.-R. F.; Bard, A. J. *Chem. Phys. Lett.* **1990**, *169*, 23.

(12) Albu-Yaron, A.; Arcan, I. *Thin Solid Films* **1999**, *185*, 181.

(13) Rollins, H. W.; Whiteside, T.; Shafer, G. J.; Ma, J.-J.; Tu, M.-H.; Liu, J.-T.; DesMarteau, D. D.; Sun, Y.-P. *J. Mater. Chem.* **2000**, *10*, 2081.

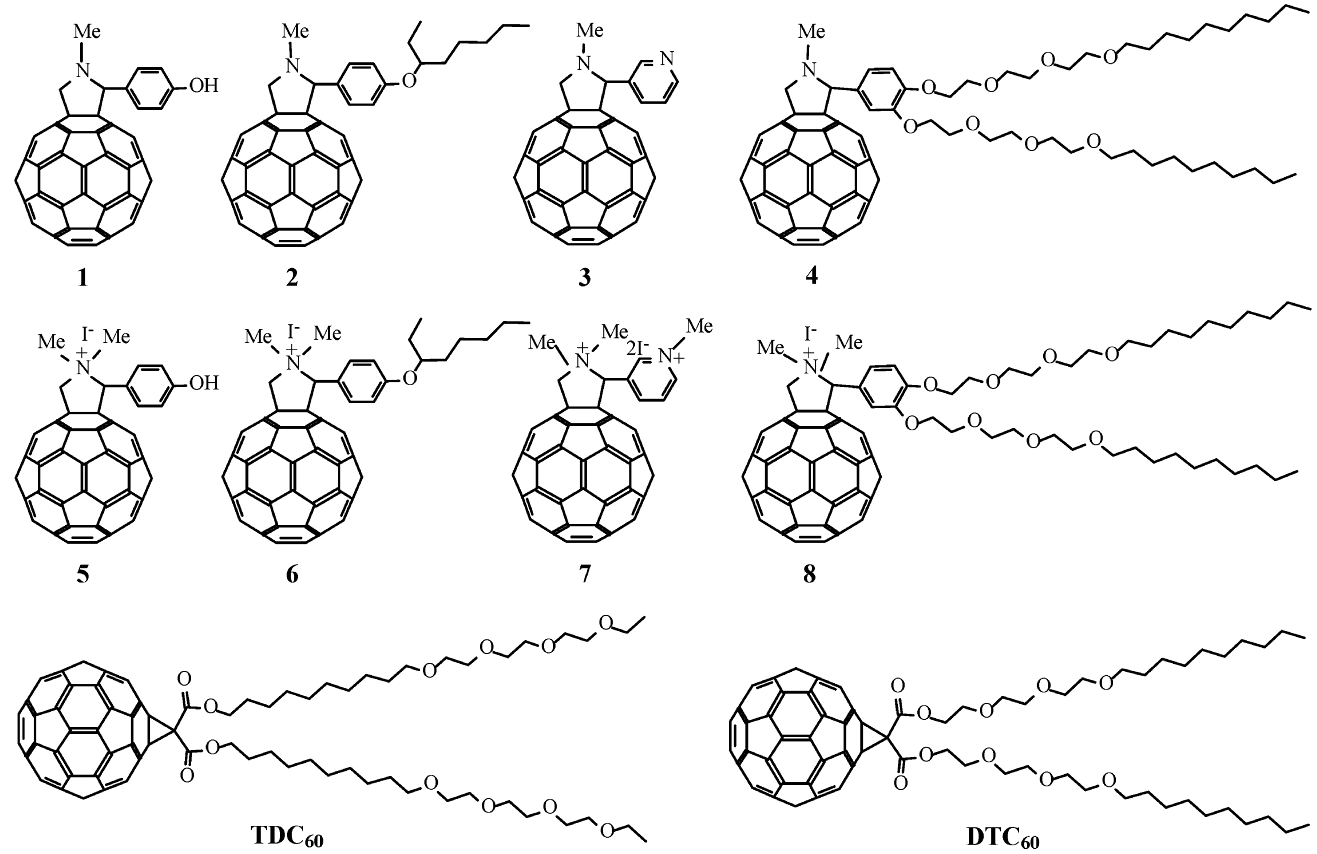
(14) Rollins, H. W.; Lin, F.; Johnson, J.; Ma, J.-J.; Liu, J.-T.; Tu, M.-H.; DesMarteau, D. D.; Sun, Y.-P. *Langmuir* **2000**, *16*, 8031.

(15) Liu, P.; Bandara, J.; Lin, Y.; Elgin, D.; Allard, L. F.; Sun, Y.-P. *Langmuir* **2002**, *18*, 10398.

(16) Guo, Z.-X.; Sun, N.; Li, J.; Dai, L.; Zhu, D. *Langmuir* **2002**, *18*, 9017.

10.1021/cm034493t CCC: $25.00

Scheme 1



structures was synthesized and incorporated into Nafion membrane to form nanoscale aggregates through a proposed hydrophilic−hydrophobic interaction between those polar groups surrounding the hollow cavities in the Nafion membrane. The aggregates showed an average size of ∼5 nm and exhibited interesting optoelectronic properties. For example, a significant optical-limiting capability was observed at a wavelength of 532 nm on a nanosecond Nd:YAG pulse laser system. However, other methanofullerenes even with similar structures (e.g., methanofullerene with inner hydrophilic chains and peripheral hydrophobic chains such as DTC$_{60}$, Scheme 1) as well as pristine C$_{60}$ could not be incorporated into Nafion membrane even after long soaking time. To further investigate the optoelectronic properties of fullerene−Nafion nanocomposites, a general method is needed to incorporate a variety of fullerene derivatives into Nafion membrane.

In this paper, we report a general approach toward the formation of C$_{60}$ nanoaggregates within the cavities of Nafion membrane. A variety of fulleropyrrolidinium derivatives can be incorporated into Nafion membrane through electrostatic interactions between the fullerene cations and the anionic sulfonate groups of the Nafion membrane. This electrostatic interaction can effectively "drive" the fulleropyrrolidinium cations into the hollow cavities of a Nafion membrane. The fullerene aggregates thus formed have a comparable size of 5−10 nm in diameter, comparable to the cavities of the Nafion membrane. Their absorption spectra are extended to the near-IR region. The fluorescence spectra are also red-shifted due to the formation of excimers. While the fulleropyrrolidinium-incorporated Nafion membrane films show strong optical limiting at 532 nm, they also limit the laser light at 1064 nm on a nanosecond Nd:YAG pulse laser system, demonstrating their potential as broadband optical limiters.

Experimental Section

Materials. Four [60]fulleropyrrolidines **1**−**4** were used to make the corresponding [60]fulleropyrrolidiniums **5**−**8** (Scheme 1). The pyridine-substituted [60]fulleropyrrolidine **3** was synthesized according to a literature method.[17] The synthesis of the other three [60]fulleropyrrolidines will be reported elsewhere.[18] The purity of each of the four [60]fulleropyrrolidines was checked with ^{1}H NMR, ^{13}C NMR, and MS spectroscopic methods. The corresponding [60]fulleropyrrolidiniums were synthesized according to the literature methods.[19] Briefly, 5 mg of a fulleropyrrolidine derivative was suspended in 2 mL of iodomethane via sonication. The suspension was stirred for 2 days at room temperature and a precipitate was formed. The precipitated dark brown solid was collected and washed with toluene several times to remove free [60]fulleropyrrolidine, if there was any. After centrifugation, the solid was dried in vacuum at room temperature overnight.

Water was deionized. Spectrophotometry-grade organic solvents were used as received with criteria of no solvent interference on absorption and emission spectra in the wavelength region of interest. Nafion 117 (1100 EW, 117-μm thick) was purchased from Aldrich.

Activation of Nafion Membrane. The Nafion−Na$^+$ membrane was prepared according to the procedure reported before.[16] Briefly, the clean Nafion membrane was immersed in concentrated nitric acid under stirring at 60 °C for 24 h,

---

[17] D'Souza, F.; Deviprasad, G. R.; Rahman, M. S.; Choi, J. *Inorg. Chem.* **1999**, *38*, 2157.

[18] (a) Zheng, L.; Zhou, Q.; Wang, F.; Deng, X.; Cao, Y.; Yu, G.; Ning, B.; Guo, Z.-X. *Acta Chim. Sinica* **2003**, submitted. (b) Zhang, P.; Li, J.; Guo, Z.-X. Unpublished results.

[19] Bullard-Dillard, R.; Creek, K. M.; Scrivens, W. A.; Tour, J. M. *Bioorg. Chem.* **1996**, *24*, 376.

followed by washing thoroughly with deionized water. The resulting Nafion−H^+ membrane was converted into the sodium form by soaking them in a 0.1 M aqueous solution of sodium hydroxide under stirring for 24 h at room temperature, followed by washing thoroughly with deionized water until the washing liquid became neutral. The resulting Nafion−Na^+ membrane was dried in vacuum at room temperature for 3 h before use. The membrane in the sodium form was clear and optically transparent down to 200 nm.

Preparation of Fulleropyrrolidinium-Incorporated Nafion Membrane. Each of the fulleropyrrolidiniums prepared above was dissolved in methanol to form a saturated solution. The Nafion−Na^+ membrane was soaked in the solution at room temperature for a certain period of time. After washing thoroughly with methanol to remove free fulleropyrrolidinium residue, if any, the membrane was dried in vacuum at 50 °C overnight.

Characterization and Measurements. UV−vis−NIR absorption spectra were obtained using a computer-controlled Shimadzu UV-3100PC recording spectrophotometer. Emission spectra were recorded on a Spex Fluorolog-3 photon-counting emission spectrometer equipped with a 450-W xenon lamp, a Spex 600 grooves/mm dual-grating (blazed at 1000 nm) as emission monochromator and 1200 grooves/mm grating (blazed at 600 nm) as excitation monochromator. The detector is a thermoelectronically cooled detector which consists of a near-infrared-sensitive Hamamatsu R2658P photomultiplier tube operated at −1500 V. In fluorescence measurements a Schott 550-nm (KV 550) color glass sharp-cut filter was placed before the emission monochromator to eliminate the excitation scattering. For the measurement of the film samples, signals were collected in front-face geometry. Fluorescence spectra were corrected for nonlinear response by using a predetermined correction factor provided by the manufacturer. All of the experiments were done at room temperature.

Transmission electron microscopy (TEM) images were taken from ultrathin cross-sectional slices of the Nafion films on an Hitachi H-800 transmission electron microscope to ensure a clear view of the films. Briefly, the Nafion film was placed in an epoxy resin for hardening, followed by cutting on an ultramicrotome with a glass knife. TEM images taken from such a sliced sample reveal a cross-sectional view of the Nafion membrane.

X-ray photoelectron spectroscopy (XPS) measurements were performed a using ESCALab 220I-XL photoelectron spectrometer with Al Kα radiation at 1486.6 eV.

The optical-limiting measurements were performed with linearly polarized 10-ns pulses generated from a Q-switched Nd:YAG laser at 1064 or 532 nm. The spatial profiles of the pulses were nearly of Gaussian form. The pulses were split into two parts: the reflected was used as reference. The sample was measured by the Z-scan method.[20] In our experiments, the maximum incident fluence at the sample was set at 10 J/cm^2. The incident and transmitted pulse energies were detected simultaneously by using two power meters (LPE-1A) individually. The laser pulses were produced at single shots or a 10-Hz repetition rate.

Result and Discussion

The fulleropyrrolidiniums synthesized are soluble in polar solvents such as methanol and result in pale yellow solutions. When a piece of Nafion membrane was soaked in a saturated methanol fulleropyrrolidinium solution at room temperature, the fulleropyrrolidinium was incorporated into the Nafion membrane, which was accompanied by a color change from colorless to light brown in several minutes. Compared with TDC_{60},[16] each of the fulleropyrrolidiniums could be incorporated into the membrane rapidly. Further soaking could lead to a homogeneously dark brown membrane. However, none of **1**−**4** could be incorporated into the Nafion membrane under the same conditions, even after 1 week's soaking. Although **4** shows comparable solubility in methanol with that of TDC_{60}, it could not be incorporated into Nafion film either. Considering the different structures of the fulleropyrrolidines and the corresponding fulleropyrrolidiniums employed in our study, a logical deduction was that the driving force for the effective introduction of a fulleropyrrolidinium into Nafion membrane arose from the electrostatic interaction between those anionic sulfonate groups surrounding the hollow cavities in the Nafion membrane and the fulleropyrrolidinium cations.

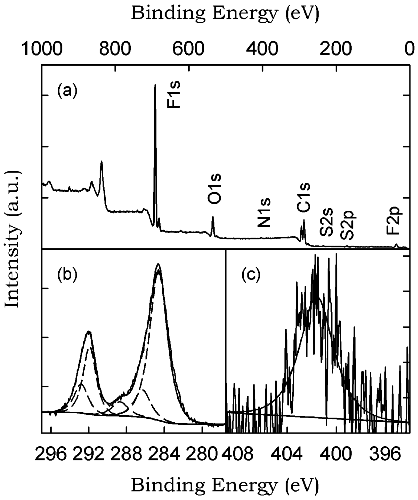


Figure 2. XPS survey spectrum (a), N 1s spectrum (b), and C 1s spectrum (c) of **5**-incorporated Nafion membrane.

The incorporation of fulleropyrrolidinium salt in the Nafion membrane was investigated by X-ray photoelectron spectroscopic (XPS) measurement. The XPS survey spectrum (Figure 2a) of the Nafion membrane incorporated with **5** for 2 days shows no peaks related to iodine, which implies that only fulleropyrrolidinium cation was incorporated into Nafion membrane, most probably through electrostatic interaction. Compared with the XPS survey spectrum of blank Nafion membrane (data not shown), there is a new peak that appears at ~401.6 eV (Figure 2b), which corresponds to the cationic nitrogen of fulleropyrrolidinium, strongly indicating the incorporation of fulleropyrrolidinium into Nafion membrane. Since the blank Nafion membrane does not contain nitrogen, the nitrogen percentage in the fulleropyrrolidinium-incorporated Nafion membrane can be used to estimate the fulleropyrrolidinium content. The 0.7% nitrogen content in **5**-incorporated Nafion membrane corresponds to ~44% (w/w) content of **5** in the Nafion membrane.

The proper curve fitting of the C 1s spectrum (Figure 2c) of **5**-incorporated Nafion film reveals the presence of F−C−O (292.82 eV) and −C−F (291.90 eV) groups, characteristic of the Nafion membrane. The peaks at 286.32 and 288.70 eV can be attributed to −C−O and −C−N^+ groups, associated with the phenol and pyrrolidinium moieties in **5**, respectively. While the blank Nafion film shows a very weak peak at 284.60 eV due to possible carbon or hydrocarbon contamination, the intensity of this peak increases significantly upon the incorporation of **5**, arising mainly from the C_{60} moiety.

---

(20) Liu, L.; Zhang, S.; Hu, T.; Guo, Z.-X.; Ye, C.; Dai, L.; Zhu, D. *Chem. Phys. Lett.* **2002**, *359*, 191.

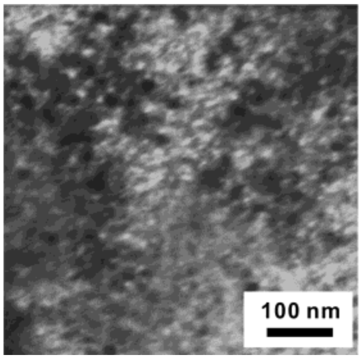


Figure 3. TEM image of **5**-incorporated Nafion membrane.

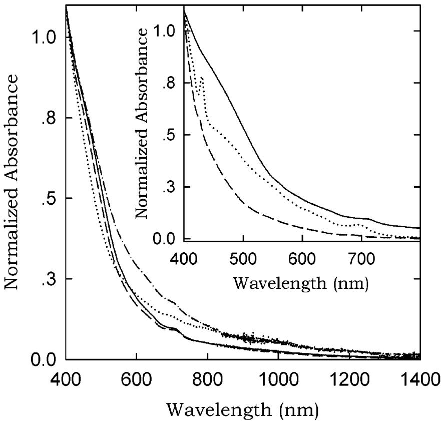


Figure 4. Absorption spectra of various fulleropyrrolidinium-incorporated Nafion membrane films. **5**-, solid line; **6**-, dashed line; **7**-, dotted line; and **8**-, dashed-dotted line. Inset shows the absorption spectra of **1** in chloroform (dotted line), **5** in methanol (dashed line), and **5**-incorporated Nafion membrane (solid line).

As expected, more direct evidence for the presence of fulleropyrrolidinium aggregates in the Nafion membrane was obtained from transmission electron microscopy (TEM). Take **5**-incorporated Nafion film for example; the aggregates formed in the film are evidenced (Figure 3) as dark spots dispersed in the brighter network-like structures associated with the perfluorinated polymer chains of the Nafion membrane.[16] A statistical analysis of dark spots yields an average spot size of 5−10 nm. This size is bigger than that of the pore size (which is ~4 nm) of the Nafion, probably due to a possible aggregation-induced expansion of the membrane pores.[16] Therefore, the size of the fulleropyrrolidinium aggregates formed within the Nafion membrane appears to be controlled by the size of the reverse micellelike ion clusters in the Nafion membrane.

The absorption spectra of fulleropyrrolidinium-incorporated Nafion membrane are shown in Figure 4. **1** shows the red onset absorption at ~710 nm and also the sharp absorption peak at ~430 nm in chloroform, which are typical absorption features of a [60]fulleropyrrolidine derivative. However, the corresponding fulleropyrrolidinium **5** gives a quite different spectrum. The characteristic absorption peak at ~430 and ~710 nm have almost disappeared, and a featureless absorption band is formed. This implies that the fulleropyrrolidiniums tend to form aggregates to some extent in methanol.[21] After **5** was incorporated into Nafion membrane, the absorption spectrum becomes much less structural; the sharp peak at ~430 nm disappears completely, which implies that the fulleropyrrolidinium is aggregated to a high level in the Nafion film compared with that in methanol solution. All of the other fulleropyrrolidinium-incorporated Nafion films also show the similar absorption results (Figure 4).

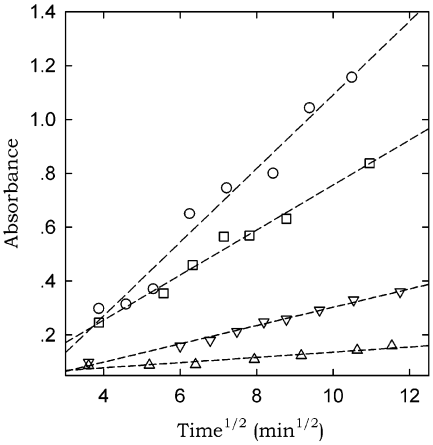


Figure 5. Absorbance at 705 nm of fulleropyrrolidinium-incorporated Nafion membrane films as a function of time$^{1/2}$. **5**-, circle; **6**-, triangle down; **7**-, square; and **8**-, triangle up.

Different from the absorbance of the fulleropyrrolidine and fulleropyrrolidinium in solution, long absorption tails are observed, extending into the near-IR region for all of the fulleropyrrolidinium-incorporated Nafion membrane (Figure 4). Such tails may be explained by the structural disorders of the fulleropyrrolidinium-incorporated Nafion films, which were also observed for the C_{60} thin films deposited on quartz substrate.[22]

The increase of the absorption of fulleropyrrolidinium-incorporated Nafion membrane with time was recorded at a wavelength of 705 nm. The absorbance increased linearly at the beginning but leveled off along with the time of soaking. The uptake of the fulleropyrrolidinium into Nafion membrane as a function of time was found to be parabolic, which could be described approximately by the following equation:[23,24]

$$Q_t = 4/l\sqrt{Dt/\pi}Q_\infty = A_t/(\epsilon l)$$

where Q_t is the concentration of the fulleropyrrolidinium in the membrane at time t, Q_∞ is the maximum concentration, D is the diffusion coefficient (cm^2/s), l is the membrane thickness, A_t is the absorbance at time t, and ϵ is the molar absorption coefficient of fulleropyrrolidinium, respectively. Plots of A_t vs $t^{1/2}$ for each of the samples investigated give straight lines (Figure 5), indicating that the incorporation of fulleropyrrolidinium into Nafion membrane is a diffusion-controlled process, which can be described by Fick's laws.[25] Thus, the smallest fulleropyrrolidinium should show the most

---

[21] Guldi, D. M.; Hungerbühler, H.; Asmus, K.-D. *J. Phys. Chem. A* **1997**, *101*, 1783.

[22] Capozzi, V.; Casamassima, G.; Lorusso, G. F.; Minafra, A.; Piccolo, R.; Trovato, T.; Valentini, A. *Solid State Commun.* **1996**, *98*, 853.

[23] Takamatsu, T.; Hashiyama, M.; Isenburg, A. E. *J. Appl. Polym. Sci.* **1979**, *24*, 2199.

[24] Mohan, H.; Iyer, R. M. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 41.

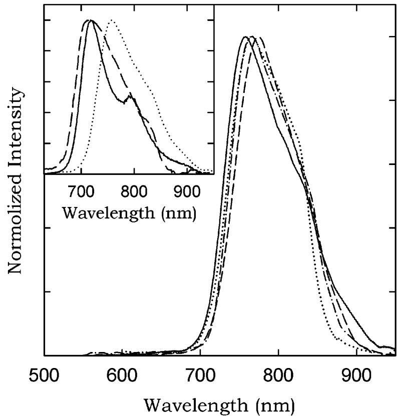


Figure 6. Emission spectra of various fulleropyrrolidinium-incorporated Nafion membrane films. **5**-, solid line; **6**-, dashed line; **7**-, dotted line; and **8**-, dashed-dotted line. Inset shows the emission spectra of **1** in chloroform (solid line), **5** in methanol (dashed line), and **5**-incorporated Nafion membrane (dotted line).

rapid incorporation speed. As calculated by Hyperchem,[26] the ascendant size sequence of the four fulleropyrrolidiniums investigated is **5** < **7** < **6** < **8**. Thus, the sequence of incorporation speed should be **5** > **7** > **6** > **8**, which is in good agreement with the experimental results.

The steady-state emission spectra of fulleropyrrolidinium-incorporated Nafion membrane were also investigated. As shown in the inset of Figure 6, **1** in chloroform shows a maximum emission at ~710 nm accompanied by a shoulder peak at ~810 nm, resembling features similar to those of methanofullerenes reported in the literature.[27] **5** in methanol gives similar features, except the emission peak is broadened. However, **5**-incorporated Nafion film shows an apparently red-shifted emission peak at ~760 nm; a shoulder peak can also be distinguished at ~820 nm. Other fulleropyrrolidinium-incorporated Nafion films also give similar results. (Figure 6) According to our fluorescence investigation of TDC$_{60}$-incorporated Nafion film reported before,[16] the red shift in the emission spectrum should be contributed to the formation of excimers via an aggregation-enhanced coupling between the adjacent excited cations within the confined geometry of the Nafion membrane, though it could also be associated with effects of the localized environment (e.g. local field effects, Stokes shift).

The controllable incorporation of fulleropyrrolidiniums into Nafion membrane can result in optically transparent uniform film. Because Nafion membrane possesses excellent processibility, chemical, thermal, and mechanical stability, these fulleropyrrolidinium-incorporated Nafion membranes are ideal membrane materials for fullerene-based optoelectronic investigation. Since C$_{60}$ and its derivatives have been reported to possess excellent optical-limiting properties,[28−30] the optical-limiting properties of fulleropyrrolidinium-incorporated Nafion membrane were investigated to construct solid optical-limiting devices. Previously, fullerene-based solid optical-limiting devices were built from fullerene-blended sol−gel glasses,[31−35] fullerene-blended polymer matrixes,[36,37] and fullerene-blended glass−polymer composites,[38] in which the relatively low solubilities of C$_{60}$ and its derivatives limited the amount of C$_{60}$ entities to be incorporated into the polymer matrixes without phase separation, and hence the optical-limiting capability. Shown in Figure 7 are the optical-limiting responses of fulleropyrrolidinium-incorporated Nafion films to 10-ns, 532-nm laser pulses from a Q-switched frequency-doubled Nd:YAG laser. To compare the optical-limiting performances, all the samples investigated were carefully prepared so that their linear transmittances at 532 nm were 50%. The optical-limiting threshold, which is defined as the input light fluence at which the output light fluence is 50% of what is predicted by the linear transmittance, is ~100 mJ/cm^2 for **5**-incorporated Nafion membrane. The optical-limiting thresholds of **6**-, **7**-, and **8**-incorporated Nafion membrane films are ~120, ~130, and ~120 mJ/cm^2, respectively. Under the same linear transmittance, **5**-incorporated Nafion

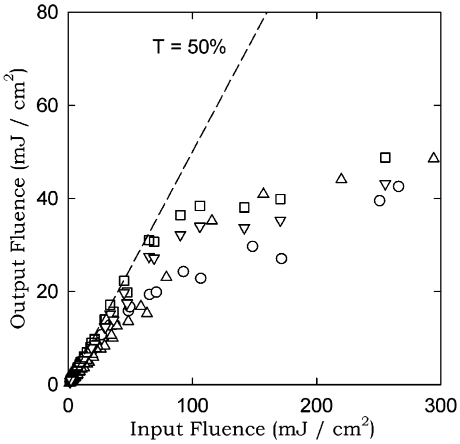


Figure 7. Optical-limiting response to 10-ns, 532-nm optical pulses of Nafion film incorporated with **5** (circle), **6** (triangle down), **7** (square), and **8** (triangle up). The linear transmittance line is 50%.

---

(25) Langsdorf, B. L.; MacLean, B. J.; Halfyard, J. E.; Hughes, J. A.; Pickup, P. G. *J. Phys. Chem. B* **2003**, *107*, 2480.

(26) *Hyperchem 7.0*; Hypercube, Inc.: 2002.

(27) (a) Luo, C.; Fujitsuka, M.; Watanabe, A.; Ito, O.; Gan, L.; Huang, Y.; Huang, C.-H. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 527. (b) Thomas, K. G.; Biju, V.; Guldi, D. M.; Kamat, P. V.; George, M. V. *J. Phys. Chem. A* **1999**, *103*, 10755.

(28) Tutt, L. W.; Kost, A. *Nature* **1992**, *356*, 225.

(29) Tutt, L. W.; Bogges, T. F. *Prof. Quantum Electron.* **1993**, *17*, 299.

(30) Sun, Y.-P.; Riggs, J. E. *Int. Rev. Phys. Chem.* **1999**, *18*, 43.

(31) (a) Schell, J.; Brinkmann, D.; Ohlmann, D.; Hönerlage, B.; Lévy, R.; Joucla, M.; Rehspringer, J.-L.; Serughetti, J.; Bovier, C. *J. Chem. Phys.* **1998**, *108*, 8599. (b) Schell, J.; Ohlmann, D.; Brinkmann, D.; Lévy, R.; Joucla, M.; Rehspringer, J.-L.; Hönerlage, B. *J. Chem. Phys.* **1999**, *111*, 5929. (c) Schell, J.; Felder, D.; Nierengarten, J.-F.; Rehspringer, J.-L.; Lévy, R.; Hönerlage, B. *J. Sol-Gel Sci. Technol.* **2001**, *22*, 225. (d) Felder, D.; Guillon, D.; Lévy, R.; Mathis, A.; Nicoud, J.-F.; Nierengarten, J.-F.; Rehspringer, J. -L.; Schell, J. *J. Mater. Chem.* **2000**, *10*, 887.

(32) Bentivegna, F.; Canva, M.; Georges, P.; Brun, A.; Chaput, F.; Malier, L.; Boilot, J.-P. *Appl. Phys. Lett.* **1993**, *62*, 1721.

(33) (a) Signorini, R.; Meneghetti, M.; Bozio, R.; Maggini, M.; Scorrano, G.; Prato, M.; Brusatin, G.; Innocenzi, P.; Guglielmi, M. *Carbon* **2000**, *38*, 1653. (b) Kordatos, K.; Prato, M.; Menna, E.; Scorrano, G.; Maggini, M. *J. Sol-Gel Sci. Technol.* **2001**, *22*, 237. (c) Signorini, R.; Meneghetti, M.; Bozio, R.; Brusatin, G.; Innocenzi, P.; Guglielmi, M.; Negra, F. D. *J. Sol-Gel Sci. Technol.* **2001**, *22*, 245.

(34) Brusatin, G.; Innocenzi, P. *J. Sol-Gel Sci. Technol.* **2001**, *22*, 189.

(35) Chollet, P. A.; Kajzar, F. *J. Sol-Gel Sci. Technol.* **2001**, *22*, 255.

(36) Riggs, J. E.; Sun, Y.-P. *J. Chem. Phys.* **2000**, *112*, 4221.

(37) Kost, A.; Tutt, L.; Klein, M. B.; Dougherty, T. K.; Elias, W. E. *Opt. Lett.* **1993**, *18*, 334.

(38) Gvishi, G.; Bhawalkar, J. D.; Kumar, N. D.; Ruland, G.; Narang, U.; Prasad, P. N.; Reinhardt, B. A. *Chem. Mater.* **1995**, *7*, 2199.

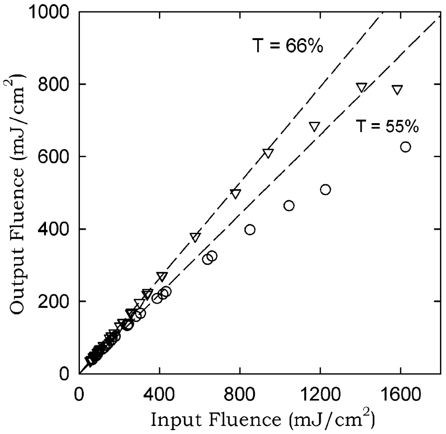


Figure 8. Optical-limiting response to 10-ns, 1064-nm optical pulses of Nafion film incorporated with **5** (circle) and **6** (triangle down).

membrane exhibits the best optical-limiting performance. It was well-established that the primary mechanism of optical limiting of solid-state C_{60} materials is reverse saturable absorption (RSA), which involves the formation of excited states with absorption cross-sectional areas much larger than the ground-state absorption cross-sectional areas under photoexcitation, therefore leading to nonlinear absorption. In the fulleropyrrolidinium-encapsulated Nafion membrane system, we suggest that the primary mechanism of the optical limiting is still RSA. In the cavities provided by Nafion membrane, a bigger molecule should becloser to its adjacent molecules. This will lead to a lower quantum yield for the intersystem crossing of the molecule from its excited singlet to triplet state, as a result of aggregation,[39,40] and resulted in less optical-limiting performances.

The measurements of fulleropyrrolidinium-incorporated Nafion films at 1064 nm also reveal optical-limiting performances. When the intensity of the laser pulses increases to ∼1.2 J/cm^2, the fluence transmitted by **5**-incorporated Nafion membrane is ∼0.5 J/cm^2 under a linear transmittance of 55%. For **7**-incorporated Nafion membrane with a linear transmittance of 66%, the fluence transmitted by the film is ∼0.7 J/cm^2 with the same laser pulses of ∼1.2 J/cm^2 (Figure 8). Thus, the fulleropyrrolidinium-incorporated Nafion membrane has the potential to be a new kind of broadband optical limiter. As fulleropyrrolidinium-incorporated Nafion films show absorption in the near-IR region (Figure 4), the mechanism for the optical limiting at 1064 nm is suggested as RSA, although other mechanisms such as nonlinear scattering[37,41] cannot be ruled out. It was reported that solution of C_{60} and its derivatives is ideal broadband optical limiters from 400 to 700 nm.[28] Our results show that, through the incorporation of fulleropyrrolidinium into Nafion membrane, its optical-limiting band could be extended to 1064 nm or even further. This result is significant for the application of fullerene derivatives for solid optical-limiting devices with broadband efficiencies.

Conclusion

In summary, a general method has been successfully developed to incorporate fulleropyrrolidiniums into Nafion membranes through electrostatic interactions between the fullerene cations and the anionic sulfonate groups of the Nafion membrane. The aggregated structures of fulleropyrrolidiniums were well-characterized by XPS and TEM methods. The absorption investigation showed that fulleropyrrolidiniums were incorporated into the Nafion membrane following a diffusion-controlled process. The formation of nanoaggregates with an average size of 5−10 nm of fulleropyrrolidiniums facilitates the excimer formation, which was evidenced by a red-shift in fluorescence emission. The resulting Nafion−fulleropyrrolidinium nanocomposites exhibit significant optical-limiting effects of practical importance at both 532 and 1064 nm, which imply their potential as broadband optical limiters to protect optical devices from damage by lasers. As fulleropyrrolidiniums and their reduced forms were reported to show enhanced electron-accepting properties[42−44] together with enhanced nonlinear optical response,[45] the fulleropyrrolidinium-incorporated Nafion membrane should find its application range from biosensor[46] to antibacterial[47] materials.

Acknowledgment. We thank Prof. Yong Cao of South China University of Technology for providing compounds **1** and **2**. This work was supported by the National Natural Science Foundation of China (Grant No. 50203015), the Major State Basic Research Development Program of China (Grant No. G2000077500), and the Chinese Academy of Sciences.

CM034493T

---

(39) (a) Venturini, J.; Koudoumas, E.; Couris, S.; Janot, J. M.; Seta, P.; Mathis, C.; Leach, S. *J. Mater. Chem.* **2002**, *12*, 2071. (b) Janot, J. M.; Seta, P.; Bensasson, R. V.; Leach, S. *Synth. Met.* **1996**, *77*, 103.

(40) Goh, H. W.; Goh, S. H.; Xu, G. Q.; Lee, K. Y.; Yang, G. Y.; Lee, Y. W.; Zhang, W.-D. *J. Phys. Chem. B* **2003**, *107* (25), 6056.

(41) Sun, Y.-P.; Riggs, J. E.; Henbest, K. B.; Martin, R. B. *J. Nonlinear Opt. Phys. Mater.* **2000**, *9*(4), 481.

(42) (a) Da Ros, T.; Prato, M.; Carano, M.; Ceroni, P.; Paolucci, F.; Roffia, S. *J. Am. Chem. Soc.* **1998**, *120*, 11645. (b) Carano, M.; Ceroni, P.; Paolucci, F.; Roffia, S.; Da Ros, T.; Prato, M.; Sluch, M. I.; Pearson, C.; Petty, M. C.; Bryce, M. R. *J. Mater. Chem.* **2000**, *10*, 269. (c) Kordatos, K.; Da Ros, T.; Prato, M.; Carano, M.; Paolucci, F.; Roffia, S. *Carbon* **2000**, *38*, 1557.

(43) (a) Guldi, D. M.; Luo, C. P.; Da Ros, T.; Bozi, S.; Prato, M. *Chem. Commun.* **2002**, 2320. (b) Guldi, D. M.; Luo, C. P.; Koktysh, D.; Kotov, N. A.; Da Ros, T.; Bozi, S.; Prato, M. *Nano Lett.* **2002**, *2*, 775.

(44) Noworyta, K.; Kutner, W.; Deviprasad, G. R.; D'Souza, F. *Synth. Met.* **2002**, *130*, 221.

(45) Koudoumas, E.; Konstantaki, M.; Mavromanolakis, A.; Couris, S.; Fanti, M.; Zerbetto, F.; Kordatos, K.; Prato, M. *Chem. Eur. J.* **2003**, *9*, 1529.

(46) Carano, M.; Cosnier, S.; Kordatos, K.; Marcaccio, M.; Margotti, M.; Paolucci, F.; Prato, M.; Roffia, S. *J. Mater. Chem.* **2002**, *12*, 1996.

(47) Bosi, S.; Da Ros, T.; Castellano, S.; Banfi, E.; Prato, M. *Bioorg. Med. Chem. Lett.* **2000**, *10*, 1043.