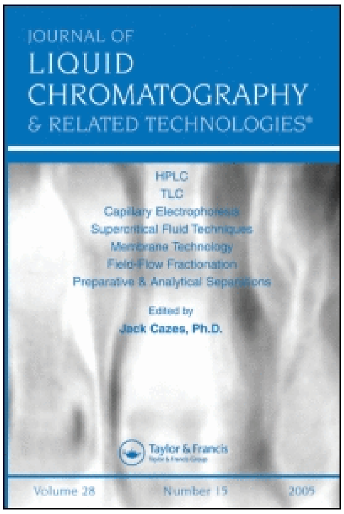
This article was downloaded by:
On: *24 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

THE HPLC SEPARATION OF FULLERENES WITH 1-METHYLNAPHTHALENE MODIFIED PSDVB RESIN

Wuyi Zha[a]; Depu Chen[a]; Weiyang Fei[b]
[a] Department of Chemistry, Tsinghua University, Beijing, P. R. China [b] Department of Chemical Engineering, Tsinghua University, Beijing, P. R. China

Online publication date: 13 January 2005

To cite this Article Zha, Wuyi , Chen, Depu and Fei, Weiyang(1999) 'THE HPLC SEPARATION OF FULLERENES WITH 1-METHYLNAPHTHALENE MODIFIED PSDVB RESIN', Journal of Liquid Chromatography & Related Technologies, 22: 16, 2443 — 2453

To link to this Article: DOI: 10.1081/JLC-100101813

URL: http://dx.doi.org/10.1081/JLC-100101813

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. LIQ. CHROM. & REL. TECHNOL., 22(16), 2443–2453 (1999)

THE HPLC SEPARATION OF FULLERENES WITH 1-METHYLNAPHTHALENE MODIFIED PSDVB RESIN

[1]Wuyi Zha,[1] Depu Chen,[2,]* Weiyang Fei

[1]Department of Chemistry
[2]Department of Chemical Engineering
Tsinghua University
Beijing 100084, P. R. China

Downloaded At: 10:18 24 January 2011

ABSTRACT

A new HPLC stationary phase, 1-methylnaphthalene modified Polystyrene-divinylbenzene resin (MNPSDVB), has been prepared to separate C_{60} and C_{70}. High column loading capacity and large separation factor of C_{60} and C_{70} were obtained in MNPSDVB column with the strong solvent, o-xylene, as the mobile phase.

INTRODUCTION

Since a new type of allotropes of carbon other than diamond and graphite, buckminsterfullerenes, C_{60}, C_{70} and higher fullerenes, were first prepared in 1990 by Krätschmer et al.[1] In macroscopic quantities based on resistive heating of carbon rods in an inert helium atmosphere, the vigorous worldwide research efforts on the fullerenes led to many important advances at a miraculous pace. The raw carbon soot prepared by resistive heating of carbon is a mixture containing the most abundant of C_{60} and C_{70}, and some higher fullerenes, such as C_{76}, C_{78}, C_{82}, and C_{84} etc.

Copyright © 1999 by Marcel Dekker, Inc. www.dekker.com

C_{60} comprises 60 carbon atoms arranged into a round, hollow and soccer-shaped molecule with the diameter of 0.7 nm, while C_{70} contains 70 carbon atoms shaped into a ellipsoid with larger molecular volume than C_{60}, about $0.7 \times 0.7 \times 0.9$ nm.[2] C_{60}, C_{70} and higher fullerenes are very similar in shapes and physicochemical properties. There are no groups on molecules that can be used for their separation. The solubility of fullerenes in many common solvents, such as water, alcohol, ether, ketone, ester, and alkane is very low. So the separation of C_{60}, C_{70} and higher fullerenes from their mixture, especially in the large scale, to prepare pure C_{60} or C_{70} seemed unsatisfactory, as it was proven to be a major throttle on the pace at which theoretical research and practical application of these compounds could proceed. In the early studies on the selective separation of C_{60} and C_{70} Hawkins et al.,[3] Welch and Pirkle,[4] and Cox et al.[5] reported similar methods on the dinitrophenyl-based (Pirkle's column) or dinitroanilino-based silica column. However, only the weakest solvent, n-hexane, could be used as mobile phase because the interaction force between fullerenes and the stationary phase was very weak, so the solubility of C_{60} or C_{70} in mobile phase was very low, only at µg/mL level, and the column loading capacity was very low. GPC column, Waters Ultrastyragel (5µm, 50nm),[2] was then used as a stationary phase for the separation of C_{60} and C_{70} with toluene as the mobile phase.

The column loading capacity was larger than that of Pirkle's column. The smaller molecule C_{60} eluted first, and followed by larger molecule C_{70} on PSDVB GPC column.[2,6]] This reversed size exclusion elution order indicated that the dominant retention mechanism of C_{60} and C_{70} is not size exclusion but the π-π interaction between fullerenes and PSDVB resins.[6]

But the interaction force between fullerenes and the stationary phase was still not so strong so that the retention of C_{60} and C_{70} on stationary phase was weak, and the separation factor was also low. Kibbey el al.[7] separated C_{60} and C_{70} on tetraphenylporphyrin modified silica gel stationary phase with toluene as the mobile phase. The high separation factor between C_{60} and C_{70} was obtained.

However, irreversible adsorption of fullerenes on the column was observed. In order to obtain high column loading capacity in the preparation separation of C_{60} and C_{70}, the stationary phases must be designed and prepared to have strong interaction force with fullerenes. Thus the retention of fullerenes on the column is strong, and strong solvent can be used as a mobile phase in which the solubility of C_{60} or C_{70} is large. In this paper, a new HPLC stationary phase, porous 1-methylnaphthalene modified PSDVB resin, was prepared for the separation of C_{60} and C_{70}.

A strong interaction force resulted from the π-π charge-transfer interaction between the fullerenes and the stationary phase made it possible to use the strong solvent, o-xylene, as the mobile phase in which fullerenes have high

Downloaded At: 10:18 24 January 2011

Figure 1. Scanning electron photomicrograph of PSDVB resins.

Downloaded At: 10:18 24 January 2011

solubility. Our column loading capacity was about 15 times higher than that of Ultrastyragel column. The separation factor of C_{60} and C_{70} was also high. Irreversible adsorption of fullerenes on the column was not observed. Large amount of C_{60} and C_{70} with high purity can be obtained with this method.

EXPERIMENTAL

Preparation of Porous PSDVB Resins

Porous polystyrene-divinylbenzene (PSDVB) resin beads were prepared by means of microsuspension polymerization from styrene and divinylbenzene in the presence of pore-producing agents, toluene and n-heptane (19/1, v/v). An aqueous solution of 1% surfactant, sodium dodecylbenzenesulphonate, containing 1% polyvinyl alcohol was used as the water dispersion phase. Volume ratio of organic phase to water phase is 1:30. The co-polymerization reaction was initiated by benzoyl peroxide and carried out at 80°C for 10 hours under vigorous stirring.

After the completion of the reaction, the product was washed, in succession, with distilling water, ethanol, and toluene, and then dried to offer white PSDVB resin beads with diameter 5-10 μm and average pore diameter 50 nm. A typical scanning electron photomicrograph of PSDVB resins was shown in Figure 1.

Chemical Modification of the Resins

The interaction force between PSDVB resins and fullerenes is very small, so that the fullerene mixture cannot be retained on the resins. Suitable separation function groups must be selected and attached to the resins. The chemical modification of resins was carried out by two successive Friedel-Crafts reactions.

A suitable reagent, such as 1,2-dichloroethane, which acts as the connecting bridge, was first connected at one end onto the resin while unreacted at another end, and then followed by the reaction between the selected modification reagent and the chloroethylized resin.

Thus, 20g dry PSDVB resins prepared were added to 30 mL 1,2-dichloroethane and the mixture was stirred to let the resins swell at 85°C for 15 min in a 100 mL flask equipped with a thermometer and a condenser. Then 15g anhydrous $AlCl_3$ was added into the slurry as a catalyst, and stirring continued for 5 min. After the completion of the reaction, 20 mL distilling water was added into the slurry to stop the reaction.

Downloaded At: 10:18 24 January 2011

The product was separated and washed, in succession, with distilling water, ethanol, acetone, and toluene, and dried to offer chloroethylized PSDVB resins. Secondly, all dried resins obtained from the first step were added to 30 mL 1-methylnaphthalene.

The mixture was stirred at 20°C for 15 min in a 100mL flask, then 15g $AlCl_3$ was added into it, and the mixture stirred for 5 min at 20°C. The following procedure was the same as was the first step. Eventually, 1-methylnaphthalene modified PSDVB resins (MNPSDVB) with diameter 5-10 μm and average pore diameter 50 nm were obtained.

Chromatographic Separation of C_{60} and C_{70} with MNPSDVB Resins

Chromatographic separation of C_{60} and C_{70} was carried out on Waters 600 HPLC with Φ4.8 × 300nm column filled with MNPSDVB resins. Waters 484 Tunable Absorbance Detector was used to monitor the separation process at the detection wavelength of 600 nm, at which low sensitivity for fullerenes was provided so as to detect peaks of C_{60} and C_{70} in high concentration.

The column was equilibrated with o-xylene until the baseline became very low and didn't change with time. 0.2 mL of mixture solution of C_{60} and C_{70} fullerenes in o-xylene was injected onto the column to study the separation property of the column. 2.00 mL sample was separated in the column loading capacity study.

Table 1

The Effect of Composition of Mobile Phase on the Separation of C_{60} and C_{70}

Mobile Phase 1-Methylnaphthalene: o-xylene(v/v)	**Flow Rate (mL/min)**	**Pressure ($/10^7$ pa)**	**Separation Factor, α**
10 : 0	0.15	1.3445	0
5 : 5	0.20	0.8067	1.44
3 : 7	0.50	0.7170	1.54
2 : 8	0.50	0.6550	1.56
0 : 10	0.50	0.3447	1.71

Downloaded At: 10:18 24 January 2011

RESULTS AND DISCUSSION

Effect of Different Compositions of Mobile Phase on the Separation of C_{60} and C_{70}

Different solvents were selected as mobile phase to separate C_{60} and C_{70} on the MNPSDVB column. Pure toluene did not elute fullerenes from the column; all C_{60} and C_{70} were adsorbed on MNPSDVB column. This shows that the interaction force between fullerenes and MNPSDVB resins is stronger than that between fullerenes and Ultrastyragel column. So, stronger solvents should be used as mobile phase instead of toluene. The mixture of toluene and o-xylene in different ratio was tested to separate C_{60} and C_{70}. They still did not elute from the column. The solubility shows the strength of interaction force between solute and solvent. The solubility of C_{60} and C_{70} in different solvents are different, for example, the solubility of C_{60} in several solvents is as follows:[8]

Solvent:	**n-Hexane**	**Toluene**	**o-Xylene**	**1-Methylnapthalene**
Solubility: (mg/mL)	0.043	2.8	5.2	33.0

The interaction force between 1-methylnaphthalene and fullerenes is the largest. So, 1-methylnaphthalene is the strongest solvent for the elution of fullerenes. But, the separation of C_{60} and C_{70} using pure 1-methylnaphthalene as mobile phase was not ideal, both C_{60} and C_{70} eluted rapidly with the solvent without any separation. At the same time, the viscosity of 1-methylnaphthalene is high, so the column pressure is very high when it is used alone as mobile phase. Then the mixtures of different ratio of 1-methylnaphthalene and o-xylene were selected as mobile phase. Table 1 shows the results of separation of C_{60} and C_{70}.

Downloaded At: 10:18 24 January 2011

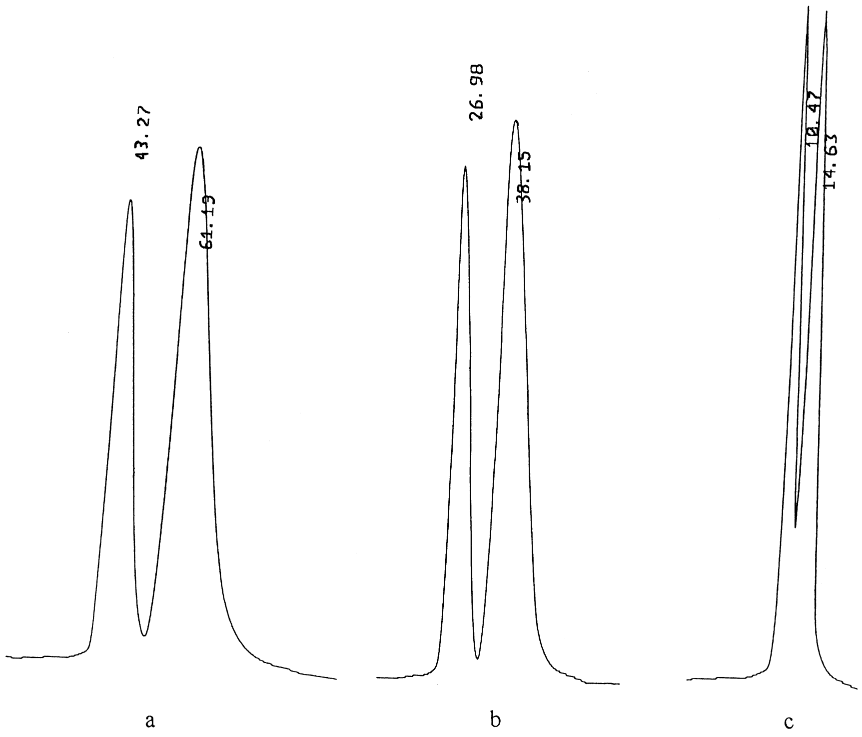


Figure 2. Chromatograph of C_{60} and C_{70} on MNPSDVB column with different flow rates. Flow rate: a. 0.25 mL/min, b. 0.4 mL/min, c. 1.0 mL/min. Sample: 0.2 mL saturated o-xylene solution of C_{60} and C_{70} (C_{60} 36%, C_{70} 63%).

The separation factor of C_{60} and C_{70} increased while the column pressure decreased with the increasing ratio of o-xylene in the mixture. Optimum separation of C_{60} and C_{70} was obtained when pure o-xylene was used as mobile phase.

Effect of Flow Rate on the Separation of C_{60} and C_{70}

C_{60} and C_{70} were separated on an MNPSDVB column with a different flow rate of o-xylene at 0.25, 0.4 and 1.0 mL/min, respectively. The chromatographic results were shown in Figure 2. When the flow rate was 1.0 mL/min, the retention times were short, and the peaks were narrow, but the peaks of C_{60} and C_{70} overlapped slightly. As the flow rate decreased, the separation of C_{60} and C_{70} became better and better as shown in Figure 2. During the separation, the pure

Downloaded At: 10:18 24 January 2011

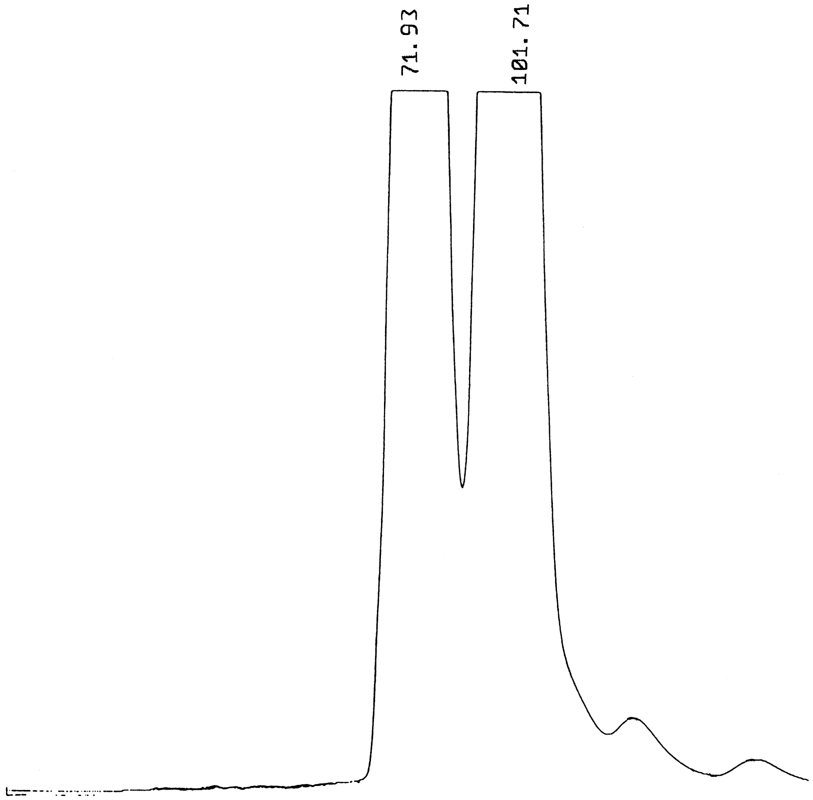


Figure 3. Chromatograph of C_{60} and C_{70} on MNPSDVB column in high loading capacity. Flow rate: 0.15mL/min; sample: 2mL saturated o-xylene solution of C_{60} and C_{70} (about 12mg mixture, C_{60} 45%, C_{70} 54%).

violet C_{60} eluted first, and followed by the yellow-brown C_{70} band. The elution order of C_{60} and C_{70} is inconsistent with size exclusion mechanism, but the same as PSDVB column.[2,6] This fact indicates that π-π change-transfer interaction between fullerene and resin dominates steric effects, and alters the elution order from a conventional size exclusion column. The separation of C_{60} and C_{70} peaks nearly reached baseline. The separation factor of C_{60} and C_{70} was 1.71. In an injection, 2.0 mL of fullerene saturated o-xylene solution (about 12mg C_{60} and C_{70}) was successfully separated in the column loading capacity test. The result was shown in Figure 3. In order to compare the separation property of MNPSDVB column with that of Ultrastyragel column, two Ultrastyragel columns (Waters, each Φ7.8mm × 300mm, particle diameter 5μm, pore diameter 50nm) were connected in series. Toluene was used as mobile phase with the flow rate of 0.25 mL/min. 1.00 mL sample of fullerenes in toluene

Downloaded At: 10:18 24 January 2011

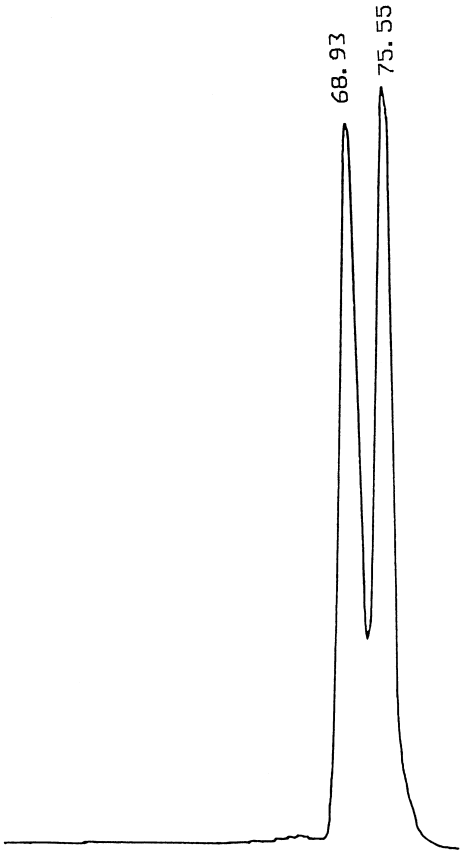


Figure 4. Chromatograph of C_{60} and C_{70} on Ultrastyragel columns. Column: two Ultrastyragel columns (Waters, each Φ7.8mm × 300mm, particle diameter 5μm, pore diameter 50nm) were connected in series; mobile phase: toluene (0.25 mL/min); sample: 1.00 mL toluene solution of fullerenes (about 3.0 mg mixture, C_{60} 36%, C_{70} 63%).

(about 3mg fullerenes) was injected into the column. C_{60} and C_{70} eluted at 68.93 min and 75.55 min, respectively. The separation factor was 1.33. It is smaller than that of MNPSDVB column, and the peaks of C_{60} and C_{70} overlapped partly as shown in Figure 4. The volume of MNPSDVB column was only 1/5 as large as Ultrastyragel column, but the loading capacity of MNPSDVB column was about 4 times as high as the later. So the total loading capacity of MNPSDVB column in the separation of C_{60} and C_{70} on preparative scale will increase by some 15 times.

Although crystallization method[9] and selective complexation of C_{60} with calixarene method[10] were reported to be able to separate C_{60} and C_{70}, it is difficult to obtain high purity C_{60} or C_{70} (>99.99%). HPLC is an ideal method to prepare highly pure C_{60} and C_{70}. MNPSDVB column shows high column loading capacity and good separation factor. It could have more practical value in the preparation of high purity of C_{60} and C_{70}.

Discussion of Separation Mechanism

HPLC separation of C_{60} and C_{70} is based on the difference of distribution ratio of C_{60} and C_{70} between stationary phase and mobile phase. To increase column loading capacity of fullerenes, it is necessary to increase the interaction force between fullerenes and stationary phase so that stronger solvents can be used as mobile phases, and the solubility of C_{60} and C_{70} in the mobile phase increases. With Pirkle's column as stationary phase, the separation mechanism of C_{60} and C_{70} involved a proposal that π-acid stationary phase containing dinitrophenyl group increased the retention action and promoted the discrimination of fullerenes which were considered as stronger π-basic aromatic clusters.[4]

However, later researches[11] indicated that C_{60} and C_{70} are not π-bases, but rather stronger electron-deficient π-acid. The electrons on C_{60} molecule delocalized poorly. The double-bond reactivity of C_{60} resembles that of very electron-deficient arenes and alkenes. It reacts readily with electron-rich reagents,[12] so it is difficult for C_{60} and C_{70} to form strong charge-transfer π-complexes with dinitrophenyl group modified stationary phase (electron-deficient π-acid). In fact, although C_{60} and C_{70} were separated with 2,4-dinitrophenyl-based silica, interaction force between fullerenes and Pirkle's stationary phase was so weak that only the weakest solvent, n-Hexane, must be used as mobile phase, while stronger solvents, such as o-xylene, cannot be used. So it is important to prepare stationary phase modified with electron-donating groups that can strengthen the interaction force between stationary phase and fullerene.

1-Methylnaphthalene is a polycyclic arene with electron-donating methyl group being attached to the ring. It should behave as a strong electron-donating property. In fact, the solubility of fullerene in 1-methylnaphthalene is very high, showing stronger interaction force between fullerene and 1-methylnaphthalene molecule. A series of C_{60} solutions in different solvents were prepared and their UV-spectra were determined. The results showed that character wavelength of C_{60} is 327.5nm in n-hexane, 334.5nm in toluene, 335.5nm in o-xylene, 344nm in 1-methylnaphthalene, respectively. The UV absorption peak of C_{60} appeared as the largest "red shift" in 1-methylnaphthalene, indicating the formation of charge-transfer complex between electron-donating 1-methylnaphthalene and electron-drawing C_{60}. We modified PSDVB resin with 1-methylnaphthalene to

Downloaded At: 10:18 24 January 2011

prepare MNPSDVB stationary phase in order to strengthen the interaction force between fullerene and MNPSDVB resin. As the result, the interaction force between fullerene and resin was so strong that strong solvent o-xylene can be selected as mobile phase, causing the solubility of C_{60} and C_{70} in mobile phase to increase greatly. The column loading capacity improved dominantly.

On the other hand, the electron affinity of C_{60} is different from C_{70}. This can be proven from the fact that the reduction potentials of C_{70} are more positive than that of C_{60} in Cyclicvoltammetry study,[13] which shows that the electron affinity of C_{70} is stronger than that of C_{60}. So, the retention ability of C_{70} on MNPSDVB resin is stronger than C_{60}. The separation factor of C_{60} and C_{70} increased.

REFERENCES

1. W. Krätschmer, L. D. Lamb, K. Frostiropoulos, D. R. Huffman, Nature, **347**, 354 (1990).
2. M. S. Meier, J. P. Selegue, J. Org. Chem., **57,** 1924-1926 (1992).
3. J. M. Hawkins, T. A. Lewis, S. D. Loren, A. Meyer, J. R. Heath, Y. Shibato, R. J. Sayklly, J. Org. Chem., **55**, 6250-6252 (1990).
4. C. J. Welch, W. H. Pirkle, J. Chromatogr., **609**, 89 (1992).
5. D. M. Cox, S. Behal, M. Disco, S. M. Gorum, M. Greaney, C. S. Hsu, E. B. Kollin, J. Millar, J. Robbins, W. Robbins, R. D. Sherwood, P. Tindall, J. Am. Chem. Soc., **113,** 2940-2944 (1991).
6. D. L. Stalling, K. C. Kuo, C. Y. Guo, S. Saim, J. Liq. Chromatogr., **6**, 699-722 (1993).
7. C. E. Kibbey, M. R. Savina, B. K. Parseghian, A. H. Francis, M. E. Meyerhoff, Anal. Chem., **65**, 3717-3719 (1993).
8. R. S. Ruoff, D. S. Tse, R. Malhotra, D. C. Lorents, J. Phys. Chem., **97**, 3379-3383 (1993).
9. X. Z. Zhou, Z. N. Gu, Y. Q. Wu, Y. L. Sun, Z. X. Jin, Y. Xiong, B.Y. Sun, Y. Wu, H. Fu, J. Z. Wang, Carbon (in Chinese), **32**, 935-937 (1994).
10. J. L. Atwood , G. A. Koutsantonis, C. L. Raston, Nature, **368**, 229-231 (1994).
11. P. M. Allemand, A. Koch, F. Wudl, Y. Rubin, F. Diederich, M. M. Alvarez, S. J. Anz, R. L. Whetten, J. Am. Chem. Soc., **113,** 1050-1051 (1991).

Downloaded At: 10:18 24 January 2011

12. P. J. Fagen, J. C. Calabrese, B. Malone, Science, **252**, 1160-1161 (1991).

13. Q. Xie, E. Perez-Codero, L. Echegoyen, J. Am. Chem. Soc., 114, 3978-3980 (1992).

Received June 27, 1998
Accepted February 22, 1999
Manuscript 4813

Downloaded At: 10:18 24 January 2011

Downloaded At: 10:18 24 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Order now!

Reprints of this article can also be ordered at

http://www.dekker.com/servlet/product/DOI/101081JLC100101813