Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Thermochimica Acta 430 (2005) 167–171
thermochimica acta
www.elsevier.com/locate/tca

Co-aggregation of fullerene C_{60} and thiophene in the non-aromatic solvent cyclohexene

Nicholas Yu. Borovkov*, Svetlana V. Blokhina, Alexis M. Kutepov, Natalie Sh. Lebedeva, Natalie A. Pavlycheva

Institute of Solution Chemistry, Russian Academy of Sciences, 1 Akademicheskaya Street, Ivanovo 153045, Russia

Received 12 August 2004; received in revised form 12 January 2005; accepted 18 January 2005
Available online 16 February 2005

Abstract

Co-aggregation of fullerene C_{60} and thiophene has been studied calorimetrically in cyclohexene at 25 °C. The total aggregation heat is found to depend on initial concentration of thiophene and fall between -1.9 and $-5.8\,\mathrm{kJ\,mol^{-1}}$. The corresponding thiophene/fullerene molar ratio ("co-aggregation number") ranges from 7 to 12. The data are rationalized by formation of heteromolecular nanoaggregates with intermolecular contacts of both fullerene–thiophene and fullerene–fullerene types. A physical model describing interaction between fullerenes and π-donors in solution is substantiated and used to explain heterogeneity of composites containing fullerenes.

Keywords: Fullerene; C_{60}; Thiophene; Aggregation

1. Introduction

Composites of fullerenes and aromatic π-donors are known to be promising photonic materials for solar cells [1]. However, manufacture of the homogeneous composites is hindered by homomolecular aggregation, i.e. formation of fullerene nanoaggregates with intermolecular contacts of the fullerene–fullerene type. Therefore it is of particular importance to study intermolecular interactions of fullerenes in liquid organic media containing such π-donors that are promising from the applied viewpoint.

Though aggregation in solution is an inherent feature of fullerenes [2], direct revealing thereof is a challenging work. At first, the study on solutions of fullerene C_{60} by vapor pressure osmometry [3] showed a lack of aggregation in toluene and partial dimerization in chlorobenzene. Then the workers [4,5] registered the nanoaggregates in benzonitrile but not in benzene by UV–vis spectroscopy and light scattering technique. At the same time, the nanoaggregates with the size of ca. 2.4 nm were registered in toluene by photoluminescence spectroscopy at low temperatures [6]. Later, these data were fully confirmed by the X-ray scattering study on solutions of fullerene C_{60} in *o*-xylene at 25 °C [7]. Thus, the most probable state of fullerene C_{60} in aromatic hydrocarbons should be considered as an aggregated one, the size of nanoaggregates and the aggregation number being of ca. 2 nm and 3–4, respectively [6,7]. However, the problem seems to be not yet fully resolved because aggregates of ca. 90 nm size have been found recently in carbon disulphide [8].

Spectroscopy and scattering techniques allow acquisition of data merely on the size of inhomogeneities in liquid media; therefore, composition and the structure of the nanoaggregates were discussed in the works [4–9] speculatively. Number of workers [4,5,9] thought a solvent could not participate in aggregation that occurred allegedly according to the equation $n\mathrm{C}_{60} \leftrightarrow (\mathrm{C}_{60})_n$. The workers [7] guessed inclusion of the solvent molecules into the nanoaggregates to be possible in one or another way. In contrast, data on mixtures of fullerene C_{60} with benzene and its derivatives acquired by thermochemical techniques were interpreted as unambiguous evidence of co-aggregation of the fullerene and π-donors in solution. The solid solvates were isolated and widely studied [10]. They were found to be fairly stable and characterized

---

* Corresponding author. Tel.: +7 932 351545; fax: +7 932 336237.
E-mail address: nyb@isc-ras.ru (N.Yu. Borovkov).

0040-6031/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2005.01.053

typically by the donor/fullerene molar ratio N of 4. Metastable forms with $N < 2$ were also revealed [11].

However, if UV–vis spectra of fullerenes in inert solvents added with methylbenzenes [8,12] are taken into account, inclusion will seem to be even a more powerful factor of aggregation than one expects from the work [10,11]. Indeed, methylbenzenes cannot cause homomolecular aggregation when added to solutions of fullerenes in such moderately effective solvent as carbon tetrachloride. However, addition thereof results in spectral changes, which are close to ones due to aggregation of fullerenes benzonitrile [4,5]. Because the changes are observed at the N values of 10^4 to 10^5, formation of the heteromolecular aggregates with a large quantity of guest π-donor molecules seems to be the most probable in these triple systems.

Recently titration calorimetry has been fruitfully used to study a triple system consisting of fullerene C_{60}, an inert solvent and such a typical π-donor as aniline [13]. The fullerene–aniline interaction has been found to be non-stoichiometric, co-operative and thus, indicative of heteromolecular aggregation rather than formation of a molecular complex. The present work has been planned as a further step to understand the fullerene–donor interactions in solution. It seeks to extract meaningful information on the initial stage of co-aggregation of fullerene C_{60} and thiophene through measuring of the aggregation heat over a wide range of the donor/fullerene ratio and discussion of data on aggregation acquired by a variety of techniques.

2. Experimental

Fullerene C_{60} (99.5%) was purchased from Astrin Co. (St. Petersburg, Russia). Cyclohexene and thiophene (purum, Fluka) were distilled on a Vigreux column before using. Solution of fullerene was prepared by steeping in cyclohexene at room temperature during 2–3 weeks.

The experiment was performed at 25 °C on a differential isothermal calorimeter [14]. The calorimetric heat responses were dynamically convoluted by use of the calorimeter constant and routines described earlier [15]. The experiment was planned in such a way that nearly saturated solution of fullerene C_{60} in cyclohexene was to be titrated with differently concentrated solutions of thiophene in cyclohexene (see C_F and C_T in Table 1). At first, fullerene C_{60} was titrated over a wide range of the thiophene/fullerene molar ratio N using solution of thiophene in cyclohexene with the largest concentration C_T (the first run in Table 1). Because dilution of thiophene was endothermic, the dilution heats obtained from separate and analogous dilution experiment (Fig. 1, curve 1) were subtracted from the heats obtained from the mixing of the solutions of fullerene C_{60} and thiophene (curve 2). The net heats Q_i (curve 3) were summarized and converted into the molar quantity Q. From the Q–N plot, the N value corresponding to the maximal heat of interaction was found (Fig. 2, curve 1, point b). Taking this value as an upper limit, two shorter titration runs were performed using two further solutions of thiophene in cyclohexene with minor concentrations

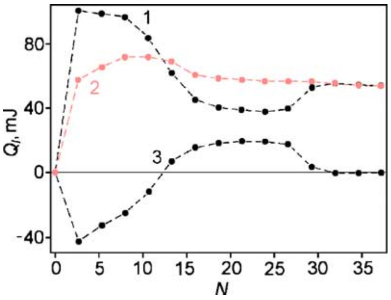

Fig. 1. Primary calorimetric data on co-aggregation of fullerene C_{60} and thiophene in cyclohexene (the first run in Table 1): (1) dilution of the solution of thiophene; (2) mixing of the solutions of fullerene and thiophene; (3) the difference concerned with the fullerene–thiophene interaction. Here Q_i stands for the heat due to injection of an ith dose of the titrant; the i value ranges from 1 to 14.

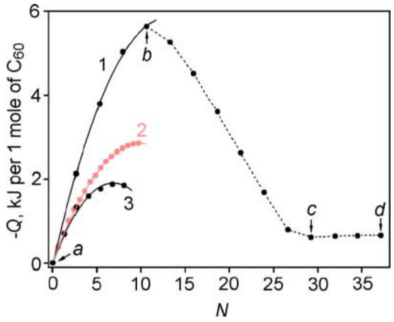

Fig. 2. The molar heats of the fullerene–thiophene interaction. The numbers correspond to No. (Table 1). The solid lines are obtained by fitting the points with the polynomial (Table 2). The physical meaning of the a–d points is explained in the text.

Table 1
Conditions of the calorimetric experiment

No.	N		C_F (mmol l^{-1})	m (g)	C_T (mmol g^{-1})	v_i (ml)	i_{max}
	Minimum	Maximum					
1	2.65	37.2	0.70	29.008	1.92084	0.0382	14
2	0.60	9.7	0.70	28.560	0.65897	0.0255	16
3	1.35	8.1	0.70	23.108	0.56700	0.0382	6

No., the run number; N, the thiophene/fullerene molar ratio; C_F and C_T, concentrations of the titrand (the solution of fullerene C_{60}) and titrant (the solutions of thiophene), respectively; m, mass of the titrand; v_i, volume of an ith dose of the titrant; i_{max}, a number of doses of the titrant added.

Table 2
Coefficients of the polynomial $Q = a + bN + cN^2$ (kJ mol^{-1}) describing the molar heat of the fullerene–thiophene interaction and positions of the maxima on the corresponding Q–N plots (solid curves in Fig. 2)

No.	a	$-b$	c	$N_{\max}$	$-Q_{\max}$
1	0.012 ± 0.045	0.907 ± 0.020	0.035 ± 0.002	12	5.8
2	−0.051 ± 0.014	0.561 ± 0.007	0.028 ± 0.001	10	2.9
3	−0.030 ± 0.061	0.550 ± 0.035	0.040 ± 0.004	7	1.9

C_T (Fig. 2, curves 2 and 3). Finally the Q–N plots were fitted with the polynomial (Table 2).

3. Results and discussion

Thiophene is chosen because its derivatives were widely studied as components of photonic materials based on fullerenes. On the other hand, thiophene is considered to be a reference π-donor for further experiments because its molecule is the smallest conventional aromatic one and devoid of lateral functional groups. Cyclohexene being one of the most effective non-aromatic hydrocarbon solvents of fullerene C_{60} is used as an inert liquid medium.

The total Q–N plot (Fig. 2, curve 1) consists of three portions demarcated by the inflection points b and c. The ab and bc portions correspond to two different stages of titration where the heat increment is positive and negative, respectively. The Q and N values found at the point b (Table 2) are dependent on titration conditions. The cd portion is parallel to the abscissa indicating the zero heat increment due to addition of thiophene at $N > 30$.

On this basis, one may conclude that there are two processes in balance, namely co-aggregation of fullerene with thiophene and disaggregation of thiophene. At low N values, the energy gained by the former is dominant and the aggregates are formed in an exothermic process. The heat increment due to co-aggregation decreases as N increases that seem to reflect a “decreasing influence” of the fullerene molecules as the aggregates become more and more filled with thiophene. At the point b, the energy gained by adding more thiophene to the heteromolecular aggregates becomes so small that it no longer outweighs the cost of disrupting the pure thiophene aggregates in solution. From this point on, any growth of the heteromolecular aggregates is inherently endothermic. Starting from the point c, no further addition of thiophene takes place because it would upset the whole balance.

Summarizing these data and ones cited above [6,7], the aggregated forms of fullerenes in solution might be sketched as follows (Fig. 3).

The simplest supramolecular unit of fullerenes seems to be a nucleus, i.e. the smallest nanoaggregate composed of few molecules of fullerene and a number of guest molecules (structures 1). Because in the solid solvates [10,11] each molecule of fullerene has contacts of the fullerene–donor and fullerene–fullerene types, both homogeneous forms with the mutually isolated molecules of fullerene (1a) and heterogeneous ones (1b) are expected in solution. Homogeneously structured nanoaggregates are not physical n-mers and therefore hardly detected by osmometry [3] and light scattering [4,5]. The nuclei may grow by two routes, namely, mutual coalescence (not shown) and further inclusion of the guest molecules. In the latter case, composition and consequently the structure of the nanoaggregates are expected to suffer changes (structures 2). Along with inclusion, solvation of the nanoaggregates resulting in formation of an outer shell should be allowed (structure 3). A kind of the shell was found in the fullerene–pyridine–water system [9].

Now the mechanism of co-aggregation of fullerene C_{60} and thiophene may be proposed. The primary exothermic stage of the fullerene–thiophene interaction (portion ab in Fig. 2) consists of nucleation, i.e. formation of the lower heteromolecular nanoaggregates with N of ca. 4 (Fig. 3, structures 1), and inclusion of the thiophene molecules (structures 2). The Q–N plot at N ranging from 0 to 12 (Fig. 2, curve 1) shows no inflection points; hence no separation of these sub-stages is possible. Inclusion stops at the point b that divides the stages of relatively strong and weak interaction between fullerene and thiophene. The corresponding $Q_{\max}$ and $N_{\max}$ values seem to have the physical meanings of the total

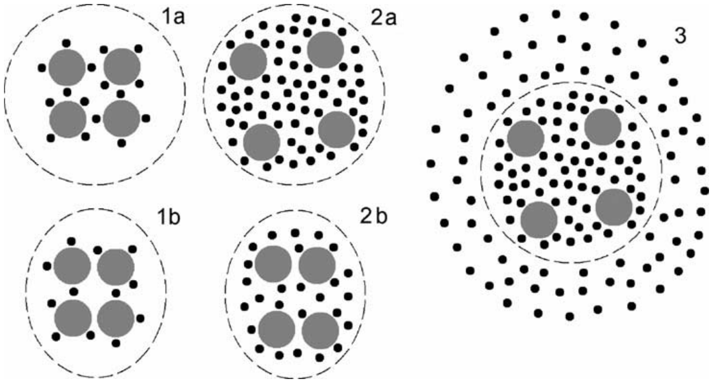

Fig. 3. Hypothetical forms of fullerene nanoaggregates in solution: (1) nucleus ((a) homogeneous; (b) heterogeneous); (2) grown forms; (3) enclosed form. Black circles stand for the π-donor molecules; the dashed lines symbolize capacity of the nanoaggregates.

aggregation heat and the limiting capacity of the nanoaggregates for thiophene (“co-aggregation number”), respectively. The curves 1–3 (Fig. 2) show that both values are dependent on experimental conditions, namely, initial concentration of thiophene in solution (C_T in Table 1).

This dependence may be rationalized as follows. Because fullerenes tend to aggregate in any solvent [2], existence of the heteromolecular aggregates of fullerene C_{60} in cyclohexene is expected as well. Consequently the fullerene–thiophene interaction should occur at not only molecular but also supramolecular level as well according to the re-solvation principle, i.e. by substitution of the guest cyclohexene molecules with the thiophene ones. At the same time, were the mechanism of co-aggregation determined only by the state of fullerene in solution, the exoeffect would depend on the C_T value inversely. The direct $|-Q|$ and C_T relationship indicates that the exoeffect arise mostly due to interaction of fullerene with the aggregated form of thiophene. When fullerene interacts with the pure thiophene aggregates, there may be a local excess of thiophene. In such a case, substitution may occur equivalently and be not accompanied by decrease in the N value and crucial changing of the supramolecular structure (Fig. 4a). When fullerene interacts with the molecular form of thiophene, substitution of the weakly π-donor and non-planar molecules of cyclohexene may occur non-equivalently and lead to a decrease in the N value (Fig. 4b). Because of partial loss of the guest molecules, the homogeneously structured nuclei should take on the heterogeneous pattern.

At the secondary stage of aggregation (portion bc in Fig. 2), interaction of the grown nanoaggregates and thiophene resulting in formation of the outer shell seems to occur. It is weakly exothermic for the following reason. To enter the shell, thiophene should be in the molecular state. Because formation of the shell is driven by the weak van der Waals forces, the heat evolved due to shell formation is too low to compensate consumption of energy due to generation of the molecular form of thiophene.

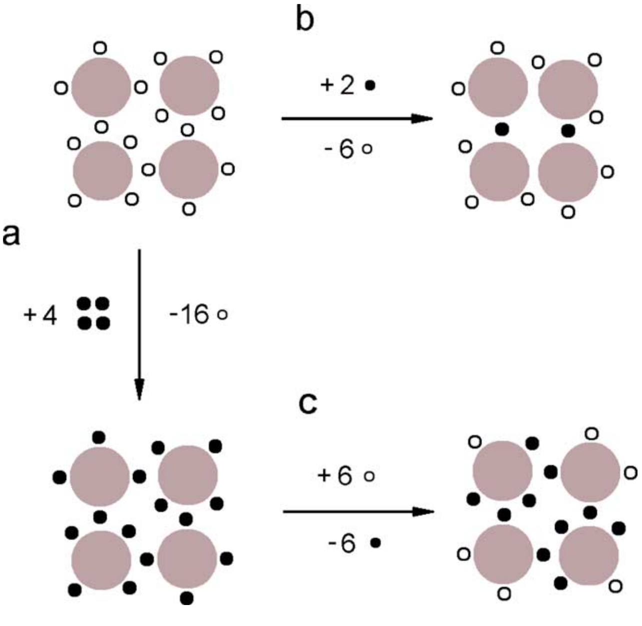

Fig. 4. Hypothetical routs of fullerene re-solvation through substitution of the guest ((a) equivalent; (b) non-equivalent) and the shell (c) molecules. Open circles stand for weaker π-donor (e.g. cyclohexene) and solid circles stand for stronger one (e.g. thiophene).

At first glance, the schemes (Figs. 3 and 4) have slight relevance to the solid fullerene–thiophene solvate (1:2) that is structured as the fullerene sublattice with the donor molecules incorporated into the free volume [16]. Such kind of crystalline structure is typical for solvates of fullerenes regardless of the molecular structure of the donor component [17–19]. It is obviously determined by geometry of the fullerene molecule and indicates – as well as the thermochemical study does – extremely small energy of interactions between the fullerene and donor molecules. The latter conclusion is strikingly evidenced by the NMR study on the solid fullerene–benzene solvate (1:4) [20] that is characterized by the largest density of the heteromolecular contacts [21–23] and seemingly the greatest contribution of the fullerene–donor interactions in stability of the whole system. In particular, benzene in the solvate is not rigidly constrained and may be exchanged, e.g. by deuterated one, without disturbing the fullerene sublattice. The benzene environment is so labile that suffers disruption due to mechanical spinning of the sample at 8 kHz [20]. Thus, from the thermodynamical viewpoint, the calorimetric and structural [16–23] data seems to be in good agreement. As for the structural viewpoint, similarity of the nanoaggregates in solution and solid state is hardly expected when a π-donor component is fairly volatile and not bound with fullerene by any significant forces!

The proposed model of co-aggregation of fullerenes with π-donors allows rational explanation of experimental discrepancies said above [3–9] and infamous heterogeneity of composites containing fullerenes [1].

A nearly mono-dispersed system of nanoaggregates is known to arise when water is added into solution of fullerene in pyridine [9]. In contrast, if a ternary system is prepared by addition of an organic solvent, two types of the nanoaggregates being remarkably different in the size arise [4]. In the former case, substitution of guest pyridine by water being devoid of π-donor properties and strongly aggregated is unfavorable thermodynamically; therefore the most probable route of interaction seems to be substitution of the shell molecules (Fig. 4c). Further aggregation occurs through mutual coalescence of the hydrated nuclei and consequently is not accompanied by collapse of their homogeneous structure. In the latter case, substitution of the guest molecules run by two routes (Fig. 4a and b) resulting in formation of the nanoaggregates both with and without the fullerene–fullerene contacts.

Despite the aggregates of fullerenes in a unary solvent consist of a few molecules, some works [5,8] reported on formation of surprisingly giant aggregated species. A common feature of both works is the forced transfer of fullerene into solution by ultrasonication of suspensions. In the light of the NMR study [20], disruption of the native homogeneously structured aggregates of fullerene by cavitation followed by coalescence due to the fullerene–fullerene contacts may be safely supposed. Here the work [24] should be mentioned where three nominally identical sample solutions of fullerene C_{60} in benzene showed different aggregation behavior. Obviously the energy barrier between the homo- and heterogeneously structured aggregates is so low that dissolution of fullerenes must be conducted under the mildest conditions to obtain reproducible experimental results.

The poly-dispersed structure of liquid systems containing fullerenes is obviously a key factor that determines heterogeneity of the fullerene–polymer composites prepared by evaporation of a volatile solvent from the triple liquid systems [1]. In solutions containing fullerene and a polymeric π-donor, both molecules of aromatic solvent and the polymer act as the guests. Because of chain rigidity, the macromolecules are weakly bound by fullerene and easily get lost during solvent evaporation. As a result, a physical mixture of the nuclei (Fig. 3, structures 1) and a free polymer is expected at the final stage of evaporation. Thus, the target composites seem to arise during the heat treatment of this mixture when the guest solvent is erratically eliminated and replaced partially by the π-donor fragments of a polymer. It is no wonder that homogeneous composites are hardly fabricated under such harsh conditions. To lower heterogeneity, application of effective but non-aromatic solvents weakly competing with the π-donor molecules in the co-aggregation process, e.g. tetrachloroethane [13] is recommended.

4. Conclusions

Co-aggregation of fullerene C_{60} and thiophene in cyclohexene has been studied by titration calorimetry. The process is characterized by values of total aggregation heat and limiting capacity of the nanoaggregates for the thiophene molecules. A physical model of co-aggregation is proposed and used to explain heterogeneity of liquid phase systems and solid composites containing fullerenes.

Acknowledgements

The work was supported by the Russian Foundation for Basic Research (Grants 01-03-33172 and 03-02-16643) and the Russian Academy of Sciences (Contract P7/03).

References

[1] A. Cravino, N.S. Sariciftci, Double-cable polymers for fullerene based optoelectronic applications, J. Mater. Chem. 12 (2002) 1931–1943.

[2] V.N. Bezmelnitsin, A.V. Eletskii, M.V. Okun, Fullerenes in solutions, Physics – Uspekhi 41 (1998) 1091–1114.

[3] R.V. Honeychuck, T.W. Cruger, Molecular weight of C_{60} in solution by vapor pressure osmometry, J. Am. Chem. Soc. 115 (1993) 3034–3035.

[4] H.N. Ghosh, A.V. Sapre, J.P. Mittal, Aggregation of C_{70} in solvent mixtures, J. Phys. Chem. 100 (1996) 9439–9443.

[5] S. Nath, H. Pal, D.K. Palit, A.V. Sapre, J.P. Mittal, Aggregation of fullerene C_{60} in benzonitrile, J. Phys. Chem. B 102 (1998) 10158–10164.

[6] J.S. Ahn, K. Suzuki, Y. Iwasa, T. Mitani, Photoluminescence of C_{60} aggregates in solution, J. Lumin. 72–74 (1997) 464–466.

[7] V.V. Golubkov, B.A. Shakhmatkin, N.A. Charykov, B.M. Aksel'rod, A study of small-angle X-ray scattering from solutions of fullerene C_{60} in *o*-xylene, Russ. J. Phys. Chem. 76 (2002) 482–485.

[8] A.D. Bokare, A. Patnaik, Evidence for C_{60} aggregation from solvent effects in [Ps–C_{60}] molecular complex formation, Carbon 41 (2003) 2643–2651.

[9] A. Mrzel, A. Mertelj, A. Omerzu, M. Čopič, D. Mihailovič, Investigation of encapsulation and solvatochromism of fullerenes in binary solvent mixtures, J. Phys. Chem. B 103 (1999) 11256–11260.

[10] M.V. Korobov, A.L. Mirakyan, N.A. Avramenko, G. Olofsson, A.L. Smith, R.S. Ruoff, Calorimetric studies of solvates of C_{60} and C_{70} with aromatic solvents, J. Phys. Chem. B 103 (1999) 1339–1346.

[11] N.V. Avramenko, E.B. Stukalin, M.V. Korobov, I.S. Neretin, Y.L. Slovokhotov, Binary systems of C_{60} with positional isomers 1,2- and 1,3-$C_6H_4Br_2$, Thermochim. Acta 370 (2001) 21–28.

[12] S. Bhattacharya, M. Banerjee, A.K. Mukherjee, Study of the formation equilibria of electron donor–acceptor complexes between [60]fullerene and methylbenzenes by absorption spectrometric method, Spectrochim. Acta A 57 (2001) 1463–1470.

[13] N. Borovkov, S. Blokhina, A. Kutepov, N. Lebedeva, M. Olkhovich, N. Pavlycheva, A. Sharapova, On the nature of interaction between fullerene and aniline, Fullerenes Nanotubes Carbon Nanostruct. 12 (2004) 583–592.

[14] N.S. Lebedeva, K. Mikhailovsky, A.I. Vyugin, A differential automatic titration calorimeter, Russ. J. Phys. Chem. 75 (2001) 1031–1034.

[15] N.S. Lebedeva, A.I. Vyugin, N.A. Pavlycheva, E.V. Parfenyuk, O.I. Davidova, Correlation between thermodynamic stability of zinc(II)tetraphenylporphyrine complexes with neutral molecules and physicochemical properties of the co-ordinated ligands, Thermochim. Acta 390 (2002) 179–186.

[16] A.D. Bond, C_{60} thiophene disolvate, Acta Cryst. E 59 (2003) o1992–o1993.

[17] C. Collins, J. Foulkes, A.D. Bond, J. Klinowski, Crystalline $C_{60}\cdot 2CHBr_3$ solvate: a solid-state study, Phys. Chem. Chem. Phys. 1 (1999) 5323–5326.

[18] M.M. Olmstead, F. Jiang, A.L. Balch, $2C_{60}\cdot 3CS_2$: orientational ordering accompanies the reversible phase transition at 168 K, Chem. Commun. (2000) 483–484.

[19] M.V. Korobov, E.B. Stukalin, A.L. Mirakyan, I.S. Neretin, Y.L. Slovokhotov, A.V. Dzyabchenko, A.I. Ancharov, B.P. Tolochko, New solid solvates of C_{60} and C_{70} fullerenes: the relationship between structures and lattice energies, Carbon 41 (2003) 2743–2755.

[20] H. He, J. Barras, J. Foulkes, J. Klinowski, Solid-state NMR studies of fullerene C_{60}/benzene solvates, J. Phys. Chem. 101 (1997) 117–122.

[21] M.F. Meidine, P.B. Hitchcock, H.W. Kroto, R. Taylor, D.R. Walton, Single crystal X-ray structure of benzene-solvated C_{60}, J. Chem. Soc. Chem. Commun. (1992) 1534–1537.

[22] H.B. Bürgi, R. Restori, D. Schwarzenbach, A.L. Balch, J.W. Lee, B.C. Noll, M.M. Olmstead, Nanocrystalline domains of a monoclinic modification of benzene stabilized in a crystalline matrix of C_{60}, Chem. Mater. 6 (1994) 1325–1329.

[23] A.L. Balch, J.W. Lee, B.C. Noll, M.M. Olmstead, Disorder in a crystalline form of buckminsterfullerene: $C_{60}\cdot 4C_6H_6$, J. Chem. Soc. Chem. Commun. (1993) 56.

[24] T. Rudalevige, A.H. Francis, R. Zand, Spectroscopic studies of fullerene aggregates, J. Phys. Chem. A 102 (1998) 9797–9802.