

π -Donors Microstructuring on Surface of Polymer Film by Their Noncovalent Interactions with Iodine

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ABSTRACT. Noncovalent (charge transfer) interaction between perylene and iodine in polycarbonate film provides formation of microstructured perylene layer on the polymer surface upon exposure of polymer film which contains dissolved perylene to solvent+iodine vapors. The prepared bilayer film possesses a sensing effect to iodine vapors which can be observed by both fluorescence and electrical conductivity changes. Similar bilayer films have been prepared also with anthracene and phenothiazine as π -donors with use of different polymer matrixes. Interaction of iodine with polycyclic aromatic hydrocarbons (PAH) has also been studied by the M06-2x DFT calculations for better understanding of phenomenon of π -donors microstructuring on surface of polymer film.

Keywords:

A. Surfaces

B. Chemical vapor deposition

C. IR, SEM

D. Fluorescence, electrical conductivity

1. Introduction

The high surface-to-volume ratio that is characteristic of either nano or submicro structures increases the amount of the surface interactions and in turn sensing properties of nano structures are significantly enhanced. This phenomenon stimulates a lot of work on engineering multi layered architectures with sensing nanolayers that use optical or electrical conductivity detection principles [1-4]

Polymer films modified by organic dyes, polycyclic aromatic hydrocarbons and their heteroanalogs have been found as perspective components for electronic and optoelectronic applications – conjugated polymer-based photovoltaic elements [5], fluorescent electron donor-acceptor pairs in polymer films under the simultaneous application of electric field and magnetic field [6], donor-acceptor polymers consisted of combination of π -electron rich and π -electron deficient conjugated moieties [7], advanced polymer materials for fluorescent solar concentrators

[8]. For example, due to their fluorescence, perylene (Fig.1) derivatives are much used in sensing compositions. Diarylethene derivatives linked to the fluorescent perylene bisimide unit have been investigated and modulation of fluorescence properties based on photochromic reactions has been noted [9]. A new calix[4]arene having pyrene and perylene moieties has been synthesized as a Na⁺-ion detecting fluorescent ionophore. When excited at the pyrene moiety (342 nm) of the ionophore, a strong fluorescence emission of the perylene moiety (at 535 nm) was observed due to energy transfer from the pyrene to perylene. By addition of Na⁺-ions at a low concentration in the range of 2.5-10 μ M, the fluorescence was remarkably quenched [10]. Moreover, perylene assembled as a monolayer is sensitive to the presence of traces amount of vapors of nitroaromatic compounds due to fluorescence quenching mechanism of the sensing [11].

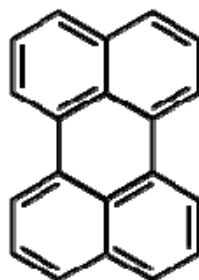


Fig. 1. Skeletal formula of perylene

Electrical resistance of perylene layer can be modulated by the proper analyte as well. It is well known that perylene interacts with iodine forming weak charge transfer complexes [12-16]. These perylene-(I₂)_n complexes were found to have an electronic conductivity 10 to 12 orders of magnitude higher than that of the constituent compounds [16], even though the ESR investigations indicates that only a minor portion of perylene is ionized with the loss of an electron in iodine melt [17a]. Therefore, perylene-(I₂)_n complexes behave themselves as valence controlled narrowband-gap semiconductors [17].

With the spotlight fixed on the development of flexible lightweight sensors, covering polymeric films with either nano or submicro structured layer of an organic π -donor (polycyclic aromatic or heteroaromatic compound, functional dye etc) may be considered as a promising approach to engineering flexible chemical sensors whose fluorescence or electrical resistance can be modulated by the proper analyte [18, 19]. In this context we suggested that a procedure being closely related to a simple synthetic method developed for surfacing polycarbonate films with conducting charge-transfer salts [20-23] may be also used for covering a polymer film with π -donor-based layer. In relation to this topic, the fabrication of polymer/peryene bilayer (BL) films as a design model of a flexible sensing material is very attractive one. The practical procedure of these BL films fabrication is based on instability of the perylene-iodine complexes on air, since the values of bonding energies of such complexes are relatively small. From these data we conclude that the perylene-(I₂)_n-based conducting layer of a polycarbonate/peryene-(I₂)_n bilayer film will not be stable and its decomposition can result in the formation of a sensitive perylene-based layer on the surface of a polycarbonate film.

Here, we report the synthetic procedure and characterization of flexible sensing bilayer films that use both fluorescence and electrical detection principles: polycarbonate/peryene, cellulose triacetate/peryene, cellulose acetate/peryene and cellulose acetate propionate/peryene. Bilayer films such as polymer matrix/anthracene and polymer matrix/phenothiazine have been prepared as well. The article also presents the M06-2x DFT calculations of the interaction energy of iodine with polycyclic aromatic hydrocarbons (PAH) that gives us an additional knowledge of how the iodine-PAH interaction provides π -donors microstructuring at the surface of polymer films.

2. Experimental

2.1. Materials. Experimental materials from ‘‘Aldrich’’, such as π -donors - perylene, anthracene, phenothiazine; polymers - pellets of Poly(Bisphenol A carbonate), (Polycarbonate, PC, average Mw ca. 64000), Cellulose Triacetate (Mw 10000), Cellulose Acetate (Mw ca. 50000), Cellulose Acetate Propionate (Mw ca. 75000) were used as received. Organic solvents – ethylacetate, 1,1-dichloroethane, benzene, toluene, 1,2-chlorobenzene, dichloromethane of analytical grade from Aldrich were used.

2.2. Covering of polymeric films with π -donors. A set of 25–30 μm thick films was prepared on glass supports at 30–40°C for 30 min and then at 100 °C for 30 min. The films comprising a 96 wt.% of either PC, or CTA, or CAP and 4 wt.% of π -donor were cast from a ethylacetate solutions. The film surfaces were treated with vapors of a saturated solution of I₂ in organic solvent during 6–8 min at 23 °C. Detailed data on the covering procedure are presented in Table S1.

2.3. Characterization of topmost π -donor layers

2.3.1. Morphology. Surface analysis on microscale was performed using a SEM ‘‘Quanta FEI 200 FEG-ESEM’’. SEM images of different magnifications were acquired at 10 kV.

2.3.2. Structure of topmost π -donor layers. X-ray powder diffraction data for bilayer films were collected in reflection mode using a Panalytical EMPYREAN instrument with a linear X'celerator detector using non-monochromated CuK_a radiation.

2.3.3. Macroscopic electro-transport properties. The values of the room temperature resistance of BL films were measured by a standard four-probe dc-method. In the case of BL films, rectangular pieces (4x2 mm²) were cut out from the film samples. Four annealed platinum wires with a diameter of 20 μm were attached to the conductive covering layer of BL films with a graphite paste [20(17a)].

2.3.4. Electronic absorption and emission spectra. Electronic absorption spectra were recorded on an APEL PD_303UV spectrometer. Fluorescence spectra were recorded on a Shimadzu on a RF-500 spectrofluorimeter.

2.4. Computational methods.

Theoretical calculations were carried out along discussion of phenomenon of π -donors microstructuring on surface of polymer film by their noncovalent interactions with iodine. For this purpose the Gaussian 03 and Gaussview 5.0 programs were used [24]. Calculations have been started from complexes with iodine above the center of each C-C bond of benzene, anthracene and perylene and optimized them via the M06-2x method [25] using a 6-311G**(d,p) basis-set [26] to find the preferred position and direction of iodine for each substrate. Complexes with the lowest energies have been reoptimized with the same method and basis set using BSSE correction. The harmonic vibrational frequencies of final complex geometries were calculated to ascertain the presence of a local minimum. Bader's atomic charges in optimized complexes at preferred geometries were calculated using the AIMAll (Version 14.06.21, Professional) program [27].

3. Results and discussion

A simple two-steps procedure has been developed to prepare bilayer polymer film (BL film) – polymer film covered by thin layer of π -donor. This procedure is illustrated in the Fig. 2 by preparation of polycarbonate film covered by crystallized layer of perylene: step 1, perylene – iodine interaction in the swollen film surface that provokes self-assembly of the perylene – iodine complex as a continuous conductive layer on the surface of a polycarbonate film and step 2, self-elimination of iodine from the above perylene – iodine complex with formation of the microstructured perylene sensing layer. The step 2 occurs regarding to the poor term-long stability of the perylene-iodine complex.

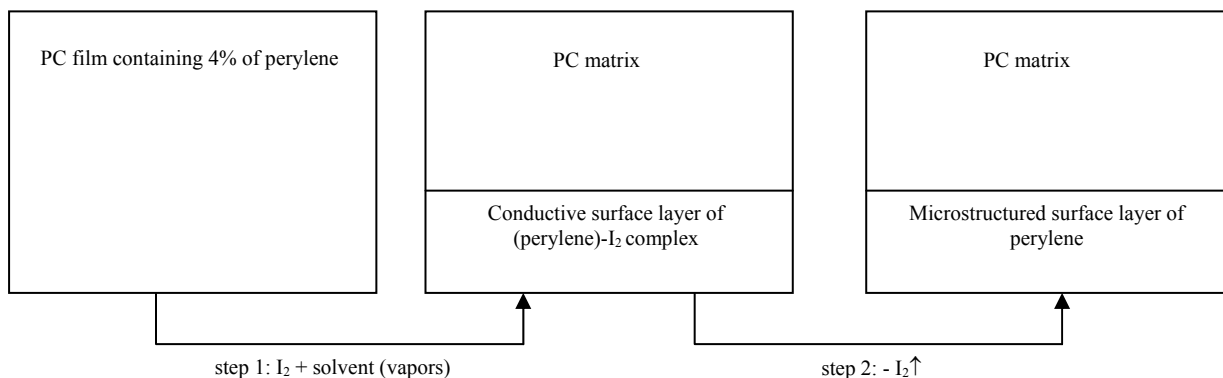


Fig. 2. Perylene microstructuring on surface of polycarbonate film by its exposure to iodine vapors.

The chemistry for self-assembling the perylene-(I₂)_n complexes (step 1, Fig. 2) is closely related to that involved for a simple synthetic method developed for metallization of polycarbonate films with organic molecular conductors. As shown in [20-23], covering of polymer film with submicro- or nanocrystallites of molecular conductor consists of one manufacture-processing step occurring at ambient conditions and includes exposition of polymer, e.g. polycarbonate, film with dissolved tetrathiafulvalene (TTF) derivative to solvent + iodine vapors. Reaction occurs in the immediate region of the swollen surface of a polymer film and leads to formation of TTF derivative - I₂ complex on the surface of polycarbonate film. This procedure has been called as “method of chemical deposition”. TTF derivatives are strong π -donors, therefore their interaction with iodine undergoes with oxidation of π -donor and formation of ionic salts. As we now have found, BL-film consisted of polymer film with covering π -donor active layer can be prepared even with much weaker organic π -donors.

Exposition of the polycarbonate film that contains dissolved perylene (4wt. %) to benzene + iodine vapors leads to definite changes in spectral properties of the film. Two bands appear in the electron absorption spectrum of the exposed film (Fig. 3, left): band at 510 nm, which is due to I₂ absorption and band at 740 nm designated to the charge transfer complex of perylene with iodine (electron absorption spectra of the perylene-iodine complexes have not been reported yet). Both these bands disappear rather fast when the exposed film is kept on the open air.

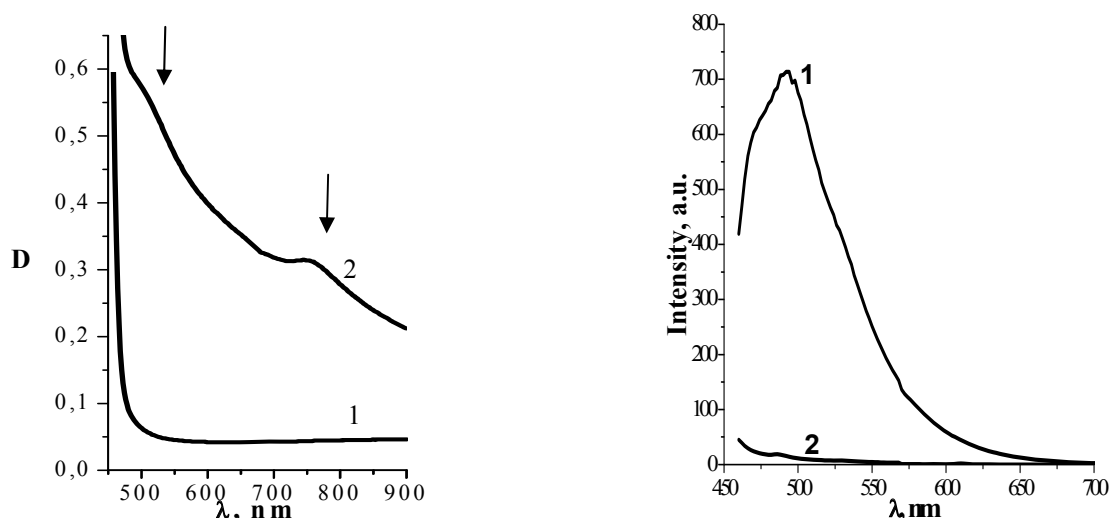


Fig. 3. Electron absorption spectra (left) and fluorescent spectra (right): 1 – polycarbonate film with dissolved perylene; 2 – polycarbonate film with dissolved perylene after exposition to solvent + iodine vapors.

Perylene fluorescence decay at 500 nm when the film is exposed to iodine vapors is also in accordance with suggestion of perylene - iodine complex formation (Fig. 3, right).

The exposed side of polycarbonate film with dissolved perylene after exposition to benzene + iodine vapors acquires an electrical conductivity. It increases during 30 min of exposition (maximal values $5-6 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$) and remains constant with longer exposition time (Fig. 4, from 30 to 40 min). It should be noted that a pure polycarbonate film has no electrical conductivity after exposition to solvent + iodine vapors. A polycarbonate film with dissolved perylene (4 wt. %) after exposition to pure solvent vapors has no electrical conductivity as well.

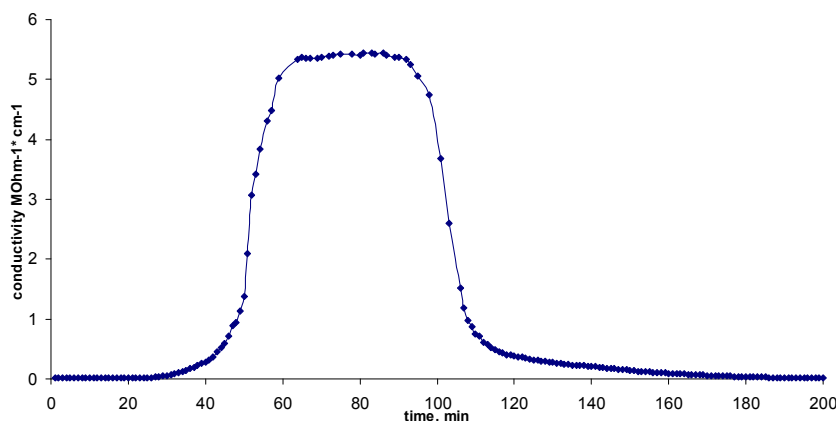


Fig. 4. Change of electrical conductivity of polycarbonate film with dissolved perylene along exposition to benzene + iodine vapors (0 - 40 min) and exposition to the open air (after 40 min).

Appearance of electrical conductivity of the polycarbonate film with dissolved perylene after exposition to benzene + iodine is due to perylene-(I_2)_n complex formation. The observed rapid loss of electrical conductivity of the PC/perylene-(I_2)_n BL film (Fig.4) is also in good agreement with earlier discussed data on the very low stability of the perylene-iodine complexes in air. The iodine desorption process (the second step Fig. 2) leads to the transformation of the crystalline perylene-(I_2)_n-based layer to the nonconductive perylene-based one and thus the PC/perylene bilayer architecture is formed.

This conclusion is proved by measuring of the attenuated total reflectance IR spectra (ATR FT IR Spectra) of the new bilayer films shown in the Fig. 5. Spectrum of perylene crystals is shown for comparison. Appearance of the perylene absorption bands at 3050, 1600, 1500,

1390, 820 and 770 cm^{-1} is observed in the ATR FT IR spectrum of the prepared perylene-polycarbonate BL-film.

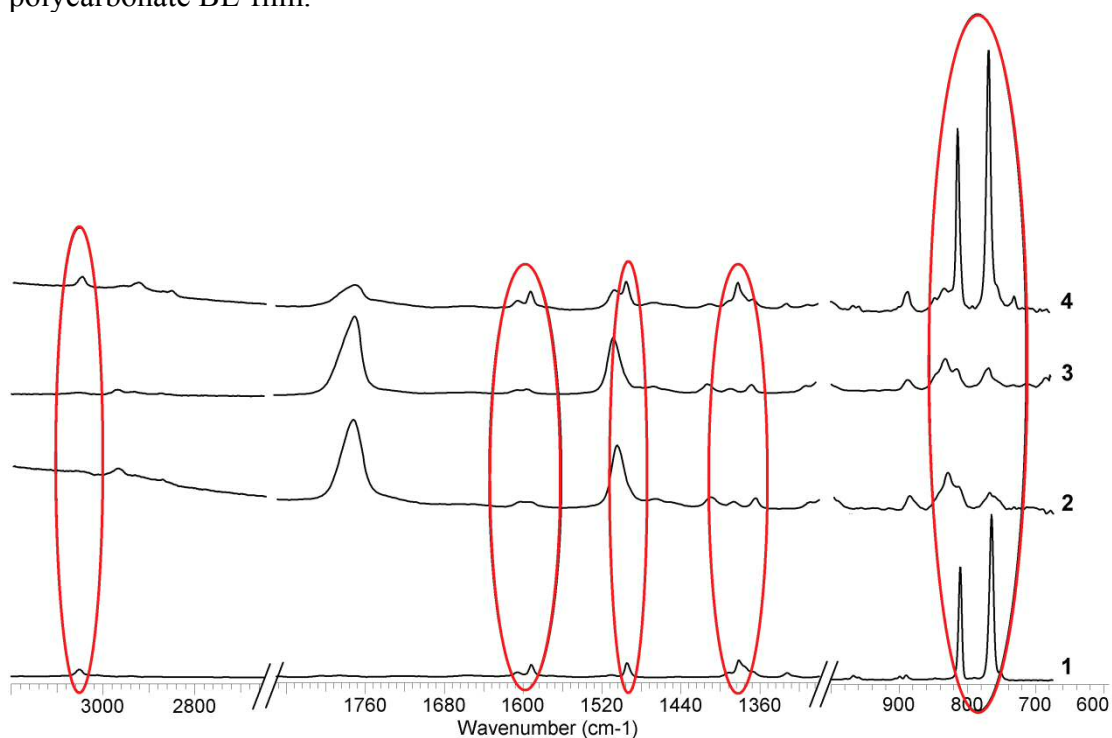


Fig. 5. ATR FT IR Spectra: 1 – perylene; 2 – polycarbonate film with dissolved perylene; 3 – polycarbonate film with dissolved perylene after exposition to benzene vapors; 4 – polycarbonate film with dissolved perylene after exposition to benzene + iodine vapors (BL-film).

We have also studied the prepared perylene-polycarbonate BL-films by scanning electron microscopy. Some of the SEM-images are shown on the Fig. 6. One can see well-structured layer of microcrystals on surface of the exposed side of polycarbonate film.

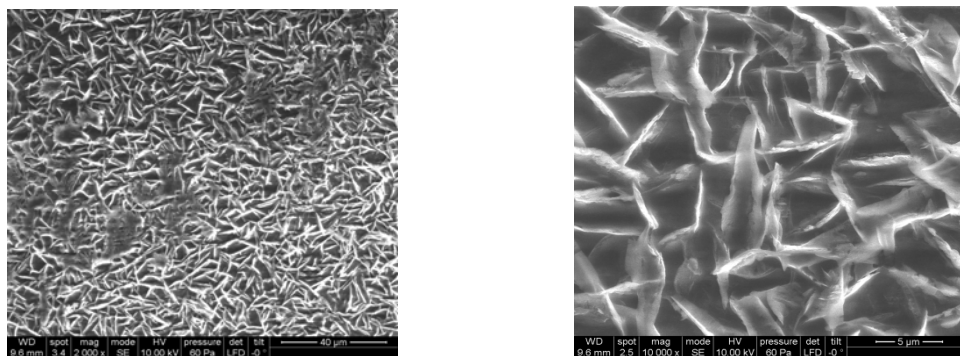


Fig. 6. SEM images of perylene - polycarbonate BL-film after 40 min exposition to benzene + iodine vapors: left is x 500; right is x 3000.

Diffraction spectrum of the perylene/polycarbonate BL-film (Fig. 7) demonstrates the diffraction lines (001, 110, 220, 22-1, 320) that are characteristic of the perylene crystal structure. This result is in accordance that the crystalline layer of perylene was formed during the second step of the BL film preparation procedure. There are no lines in the diffraction spectrum related with the perylene-iodine complexes.

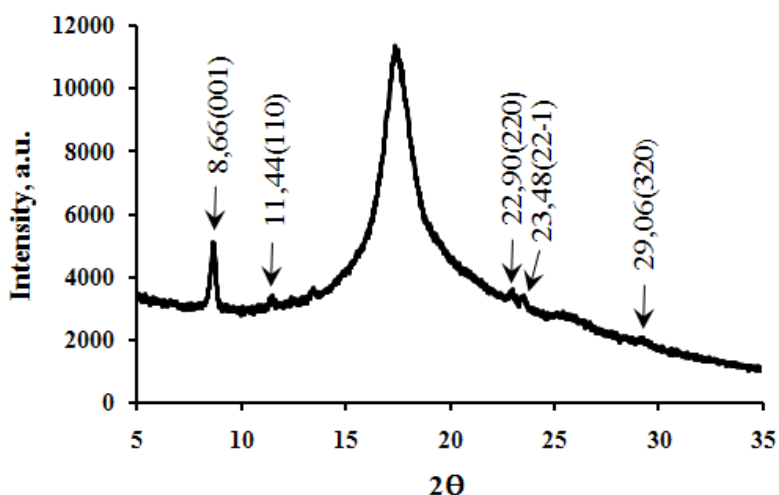


Fig. 7. The X-ray diffraction spectrum of the perylene-based layer of the BL-film.

Thus, both SEM and X-ray examinations of the surface of a reference polycarbonate film suggest the formation of the perylene-based layer on the treated side of the film.

The polycarbonate/peryene- BL-films, prepared by the described procedure are stable for a long time and can be used as a functional element. As example, we show sensing properties of these BL-films to iodine vapors. Fluorescence modulation and electrical conductivity changes come from repeated exposition of the film to iodine vapors. The BL-film which lost electrical conductivity becomes fluorescent one due to disruption of perylene-iodine complex. It losses emission again and gets electrical conductivity when exposed to iodine vapors. While comparing effects shown on Figs. 4 and 8 one can note the electrical conductivity of BL-film changes undergo much slower than its fluorescence modulation. Obviously, electrical conductivity appears after a development of the specific crystal structure of the perylene-iodine complex. This procedure takes a definite period of time. Fluorescence decay does not need the development of certain crystal structure and caused due to the external heavy atom effect [28].

Moreover, via fluorescence modulation polycarbonate/peryene BL-film behaves ability to control different duration of exposition to iodine vapors as it is shown in the Fig. 8 (exposition times are shown at minimal points of fluorescence).

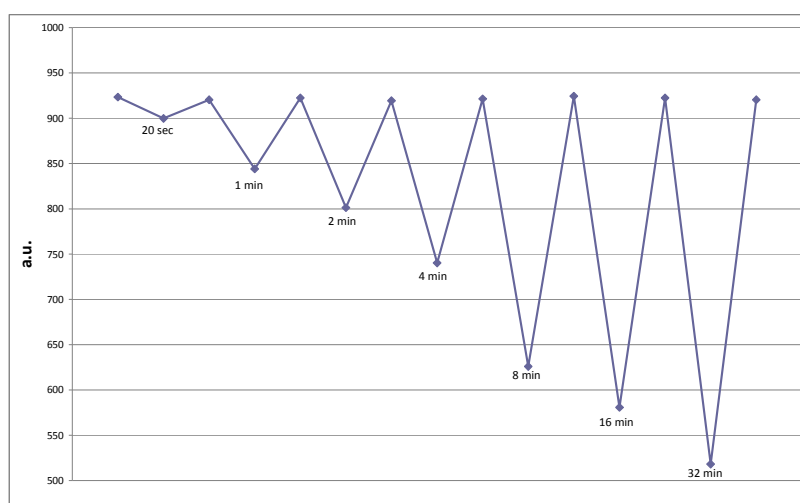


Fig. 8. Fluorescence modulation of perylene - polycarbonate BL-film after exposure to iodine vapors (minimal points) and after exposure to air (maximal points); exposition times are given at minimal points of fluorescence.

In accordance to it, polycarbonate films with dissolved perylene - both treated by pure solvent vapors and untreated ones - do not show any sensing effect to iodine vapors at all.

As we have found, besides of polycarbonate other polymer matrixes (cellulose acetate, cellulose triacetate and cellulose acetate propionate) can be also used for the preparation of sensing BL-films (Fig. 9): perylene absorption bands at 3050, 1600, 1500, 1390, 820 and 770 cm^{-1} are observed in the ATR FT IR spectrum of the BL-film.

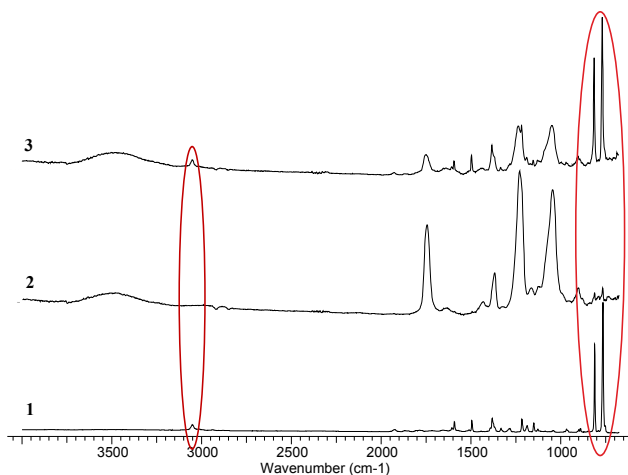


Fig. 9. ATR FT IR Spectra: 1-4% perylene in cellulose triacetate; 2 – cellulose triacetate film with dissolved perylene; 3-4% perylene in cellulose triacetate after exposure to dichloroethane+iodine vapors (30 min)

Perylene seems to be not the only π -donor that is able to form a crystalline covering layer due to its weak complexation with iodine. We have used the same experimental procedure to prepare similar BL-films faced with naphthalene, anthracene and phenothiazine, which are also known to form charge transfer complexes with iodine [29, 30]. However, these π -donors turned to be different in their ability to form polymer BL-films. Both anthracene absorption bands at 980 and 750 cm^{-1} in the ATR IR Spectra (Fig. 10A) and phenothiazine absorption bands at 3055, 815 and 760 cm^{-1} that are seen in the Fig. 10B support formation of the anthracene and phenothiazine BL-films. Nevertheless, we could not see any definite bands of naphthalene in the ATR FT IR spectrum polymer film after iodine vapors treatment of a polycarbonate film that contains this dissolved π -donor.

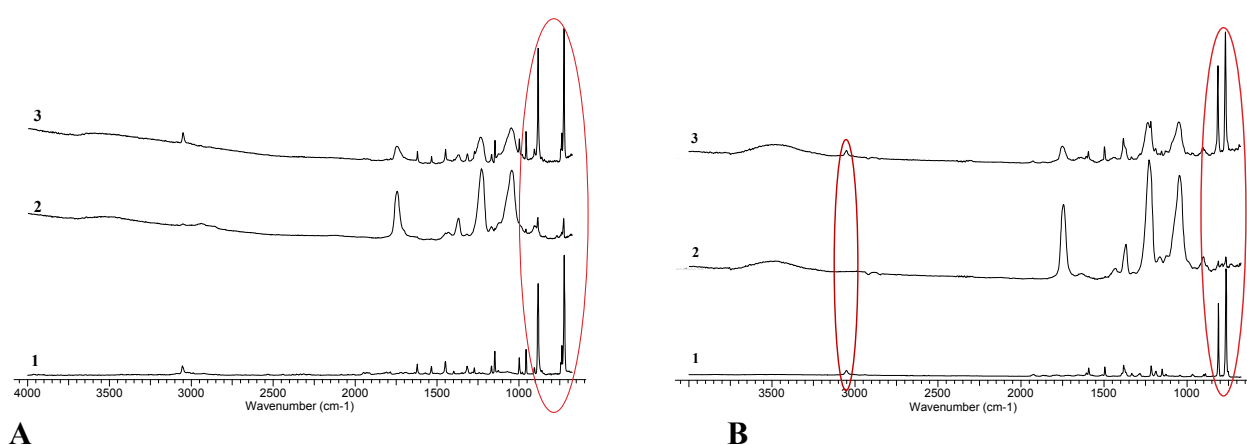


Fig. 10. ATR FT IR Spectra: **A:** 1- anthracene; 2-4% anthracene in cellulose acetate; 3-4% anthracene in cellulose acetate after exposure to dichloroethane+ iodine vapors (30 min); **B:** 1- phenothiazine; 2-4% phenothiazine in polycarbonate; 3-4% phenothiazine in polycarbonate after exposure to benzene+ iodine vapors (30 min)

As we have found, the prepared perylene, anthracene and phenothiazine BL-films differ also in their ability for sensing of iodine vapors. Both anthracene and phenothiazine seem to form too stable complexes with iodine [29, 30]. Therefore, decomposition rate of anthracene-iodine complex seems to be rather low one to provide the anthracene BL-film good sensing effect for iodine vapors. Sensing effects of the perylene and anthracene BL-films to iodine vapors are compared in the Fig. 11 (A and B respectively). The complex of iodine with phenothiazine does not desorb iodine at all.

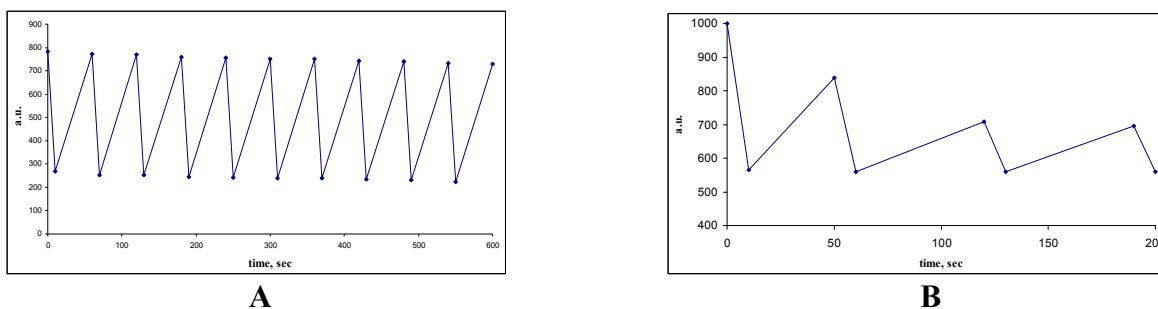


Fig. 11. Fluorescence modulations of perylene (A) and anthracene (B) - polycarbonate BL-film after exposure to iodine vapors for 10 minutes (minimal points) and after exposure to the open air (maximal points)

For better understanding of the phenomena of π -donor microstructuring on surface of polymer film and sensing ability of the proper BL films to iodine vapors, we have studied interaction of iodine with several polycyclic aromatic hydrocarbons (PAH) by quantum chemical calculations. Molecular modeling calculations at M06-2x/6-311G**(d,p) level with BSSE correction in gas phase were performed to predict possible geometries and interaction energies of iodine complexes with perylene, anthracene and benzene. We have found that geometries, where acceptor molecule is perpendicular to π -donor's plane and interacts with one of the inner carbon atoms are the most preferable ones (Fig. 12). This is in good agreement with previous (both XRD [31] and computational [32]) studies of charge transfer complexes of π -donors with halogens.

BSSE-corrected interaction energies have been found as follows: 16.64, 19.63 and 19.00 kJ/mole for benzene, anthracene and perylene, respectively. These values are also in good agreement with Yurtsever et al calculations of naphthalene-iodine interaction [32]. The stronger

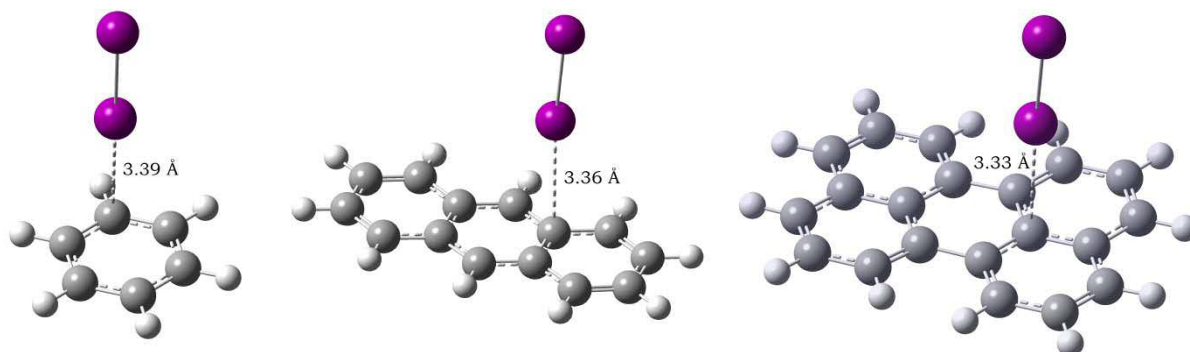


Fig. 12. Optimized structures of iodine complexes with benzene, anthracene and perylene at M06-2x/6-311G**(d,p) level with BSSE correction in gas phase.

interaction between iodine and perylene (or anthracene) provides formation of corresponding complexes on the surface of polymer film. Moreover, the highest interaction energy for iodine-

anthracene pair probably hinders observation of good sensing effect for iodine vapors by the prepared anthracene BL-film. The Yurtsever et al data of lower stability of naphthalene-iodine complex seem to explain our unsuccessful results in the naphthalene BL-film preparation.

4. Conclusion

In summary, noncovalent interaction (charge transfer complexing) between perylene and iodine that occurs in the swollen surface of polymer film results in the formation of microstructured perylene-based covering layer. The developed chemical deposition method is a very simple two-steps procedure that occurs at ambient conditions. The polycarbonate film covered with the perylene-based layer demonstrates sensitivity to iodine vapors which can be easily detected by fluorescence spectra as well as by electrical conductivity. Other polymer matrixes, e.g. cellulose acetate, cellulose triacetate, cellulose acetate propionate provide also formation of similar BL-films. Other π -donors form similar BL-films as well. Even though anthracene and phenothiazine BL-films do not show good ability for sensing iodine vapors, these BL-films can be useful in other applications. For example, phenothiazine BL-film is of interest due to good electrical conductivity of phenothiazine-iodine complex [30].

Acknowledgments

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Supporting Information Available Additional spectral data, SEM images, experimental details and procedure of polymer films preparation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- [1] S. Forrest, *Nature* 428 (2004) 911.
- [2] A. Basudam, M. Sarmishtha, *Prog. Polym. Sci.* 29 (2004) 699.
- [3] A.K. Bajpai, S.K. Shukla, S. Bhanu, S. Kankane, *Prog. Polym. Sci.* 33 (2008) 1088.
- [4] F.J. Xu, J.P. Zhao, E.T. Kang, K.G. Neoh, *Ind. Eng. Chem. Res.* 46 (2007) 4866.
- [5] N.S. Sariciftci, *Current Opinion in Solid State and Material Science* 4 (1999) 373.
- [6] M. Mizoguchi, N. Ohta, *Chemical Physics Letters* 372 (2003) 66.
- [7] J.D. Yuen, J. Fan, J. Seifert, B. Lim, R. Hufschmid, A.J. Heeger, F.J. Wudl, *Amer. Chem. Soc.* 133 (2011) 20799.
- [8] B.C. Rowan, L.R. Wilson, B.S. Richards, *IEEE Journal of Selected Topics in Quant. Elect.* 14 (2008) 1312.
- [9] T. Fukaminato, M. Irie, *Adv. Mater.* 18 (2006) 3225.
- [10] Y. Nishimura, T. Takemura, S. Arai, *ARKIVOC* xiii (2007) 259.
- [11] Sh. Zhang, F. Lu, L. Gao, L. Ding, Yu Fang, *Langmuir*, 23 (2007) 1584.
- [12] (a) E. Clar, K. Brass, *Ber.* 65 (1932) 1660; (b) A. Zinke, A. Pongratz, *Ber.* 70 (1937) 214. (c) T. Uchida, H. Akamatu, *Bull. Chem. Soc. Japan*, 34 (1961) 1015.
- [13] (a) C. Cobb, E. Wallis, *J. Phys. Chem.* 72 (1968) 2990. (b) S. Aronson, B. Strumeyer, R. Goodman, *J. Phys. Chem.* 76 (1972) 921.
- [14] O. Hassel, K.O. Stomme, *Acta Chem, Scand.* 12 (1958) 1146.
- [15] Z. Buffett, P.K. Ummat, W.R. Datars, *Physica B* 279 (1999) 341.

- [16] J. Kommandeur, F. R. Hall, *J. Chem. Phys.*, 34 (1961) 129.
- [17] (a) J. Kommandeur (1961), *Molecular Physics: An International Journal at the Interface Between Chemistry and Physics*, 4:6, 509-511, DOI:10.1080/00268976100100681.
(b) H. Akamatu, H. Inokuchi, *J. Chem. Phys.*, 18 (1950) 810.
- [18] D. Patra, A.K. Mishra, *Sensors Actuators B* 80 (2001) 278.
- [19] J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, P.L. Burns, A.B. Holmes, *Nature* 347 (1990) 539.
- [20] (a) E. Laukhina, V. Tkacheva, I. Chuev, E. Yagubskii, J. Vidal-Gancedo, M. Mas-Torrent, C. Rovira, J. Veciana, S. Khasanov, R. Wojciechowski, J. Ulanski, *J. Phys. Chem. B* 105 (2001) 11089; (b) E. Laukhina, C. Rovira, J. Ulanski, *Synth. Met.* 121 (2001) 1407.
- [21] (a) E. Laukhina, V. Merzhanov, S. Pesotskii, A. Khomenko, E. Yagubskii, J. Ulanski, M. Kryszewski, J. Jeszke, *Synth. Met.* 70 (1995) 797; (b) E. Laukhina, J. Ulanski, A. Khomenko, S. Pesotskii, V. Tkachev, L. Atovmyan, E. Yagubskii, C. Rovira, J. Veciana, J. Vidal-Gancedo, V. Laukhin, *J. Phys. I France* 7 (1997) 1665.
- [22] (a) V. Laukhin, R. Pfattner, M. Mas-Torrent, E. Laukhina, C. Rovira, J. Veciana, *International Conference EUVROSENSORS XXII- 2008*, Dresden, Germany, Book of Abstract, 2008. (b) E. Laukhina, M. Mas-Torrent, C. Rovira, J. Veciana, V. Laukhin, P200602887 (WO2008059095), Spain, 2006.
- [23] A. Tracz, A. Mierczynska, K. Takimiya, T. Otsubo, N. Nihara, J.K. Jeszka, *Materials Science-Poland*, 24 (2006) 517.
- [24] M.J. Frisch, G.W. Trucks, H.B. Schlegel et al. *Gaussian 03*, Revision E.01, Gaussian, Inc., Wallingford CT, 2004.
- [25] Y. Zhao and D.G. Truhlar, *Theor. Chem. Account.* 120 (2006) 215.
- [26] (a) R. Krishnan, J.S. Binkley, R. Seeger and J.A. Pople, *J. Chem. Phys.* 72 (1980) 650;
(b) M.N. Glukhovstev, A. Pross, M.P. McGrath, L. Radom, *J. Chem. Phys.* 103 (1995) 1878.
- [27] T.A. Keith, TK Gristmill Software, Overland Park KS, USA, 2014.
- [28] Y. Shimizu, T. Azumi, *J. Phys. Chem.* 86 (1982) 22.
- [29] N. Gogulamurali, S.A. Suthanthiraraj, P. Maruthamuthu, *Journal of Materials Science*, 27 (1992) 98.
- [30] R.A. Singh, R.K. Gupta, S.K. Singh, *Bull. Mater. Sci.*, 28 (2005) 423.
- [31] A.V. Vasilyev, S.V. Lindeman, J.K. Kochi, *Chem. Commun.*, (2001) 909.
- [32] B. Sütay, M. Yurtsever, E. Yurtsever, *J. Mol. Model.*, (2014) 20:2445.