Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2016, 26, 149–151

Mendeleev Communications

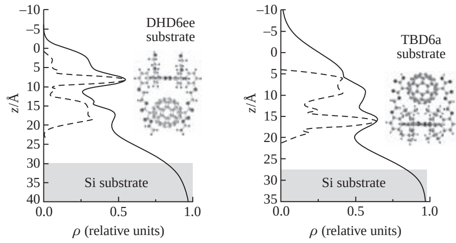
Orientation of donor–acceptor dyad molecules in Langmuir–Schaefer monolayers revealed by X-ray reflectometry

Yulia A. Dyakova,*[a,b] Margarita A. Marchenkova,[a,b] Alexey Yu. Seregin,[a,b] Lala R. Imamova,[a]
Elena Yu. Tereschenko,[a,b] Vera V. Klechkovskaya,[a] Alexander S. Alekseev[c] and Mikhail V. Kovalchuk[a,b]

[a] A. V. Shubnikov Institute of Crystallography, Russian Academy of Sciences, 119333 Moscow, Russian Federation. Fax: +7 499 135 1011; e-mail: juliaadi@gmail.com
[b] National Research Centre ‘Kurchatov Institute’, 123182 Moscow, Russian Federation
[c] A. M. Prokhorov General Physics Institute, Russian Academy of Sciences, 119991 Moscow, Russian Federation

DOI: 10.1016/j.mencom.2016.03.023

Donor–acceptor dyads are very promising compounds for low-cost organic photovoltaic devices. The orientation of porphyrin–fullerene dyads TBD6a and DHD6ee formed on a solid substrate by the Langmuir–Schaefer method is considered. It was shown by X-ray reflectivity that molecular orientation persisted during that transmission from liquid to solid surface in spite of the dyad molecules low anisometry.



The development of new compounds for low-cost organic photovoltaic devices is in demand for materials science.[1–5] Structural studies are among the most important steps to solve the problem of increasing the efficiency of photovoltaic devices since they allow one to carry out the desired correction of the material synthesis, methods of preparing and conditions of the active layer formation.

The porphyrin–fullerene dyads 61,62-[10,20-(3,5-di-*tert*-butylphenyl)porphyrin-5,15-diylbis(1-phenyl-3-hydroxy)diethylene] 1,9:49,59-bismetano[60]fullerene-61,61,62,62-tetracarboxylate (TBD6a) and 61,62-diethyl-{10,20-[3-(2-hydroxyethoxy)phenyl]-porphyrin-5,15-diylbis(1-phenyl-3-oxy)diethylene} 1,9:49,59-bismetano[60]fullerene-61,61,62,62-tetracarboxylate (DHD6ee) studied in this work consist of electron-donor (porphyrin) and electron-acceptor (fullerene) parts covalently linked to each other by two hydrocarbon chains (Figure 1). Under photoexcitation, the electron from a donor moves to an acceptor, thereby effecting directed intramolecular charge transfer. The small distance between donor and acceptor provides the relatively long lifetime of the charge-separated state, which makes these molecules promising components of active layers in photovoltaic cells.[6] For the dyad layers to show high photo efficiency the molecules should be arranged in a similar orientation relative to the surface. Previously,[7–9] the photovoltaic characteristics of dyad films were studied but conclusion about orientation of molecules was made based on their electrophysical properties. In the present work, orientations of the TBD6a and DHD6ee molecules were examined from the structural point of view by X-ray reflectivity.

Recently, the orientation of the dyads doped by metal ions (ZnDHD6ee) was investigated in the monolayers on the liquid subphase surface and on the solid substrates by the method of X-ray standing waves.[10] It was shown that the dyads ZnDHD6ee

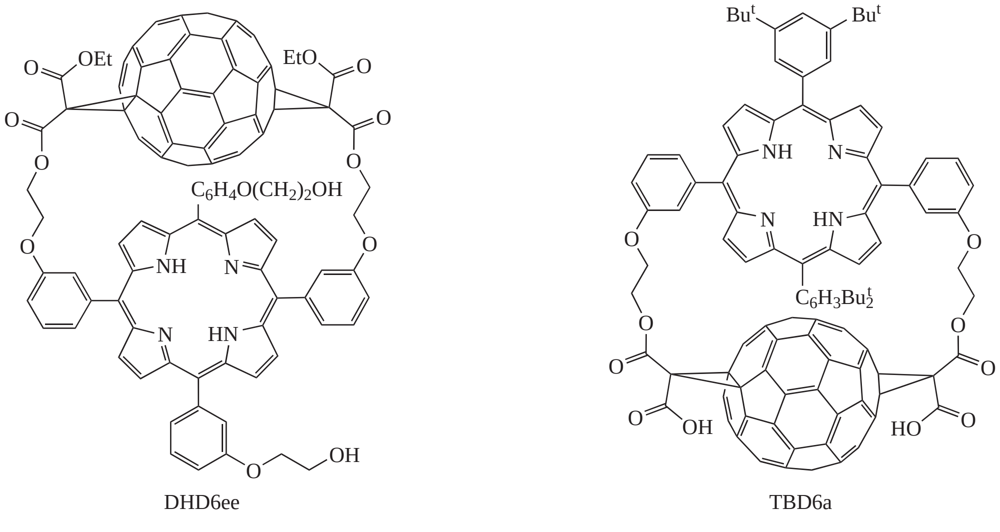


Figure 1 Structures of the porphyrin–fullerene dyads DHD6ee and TBD6a.

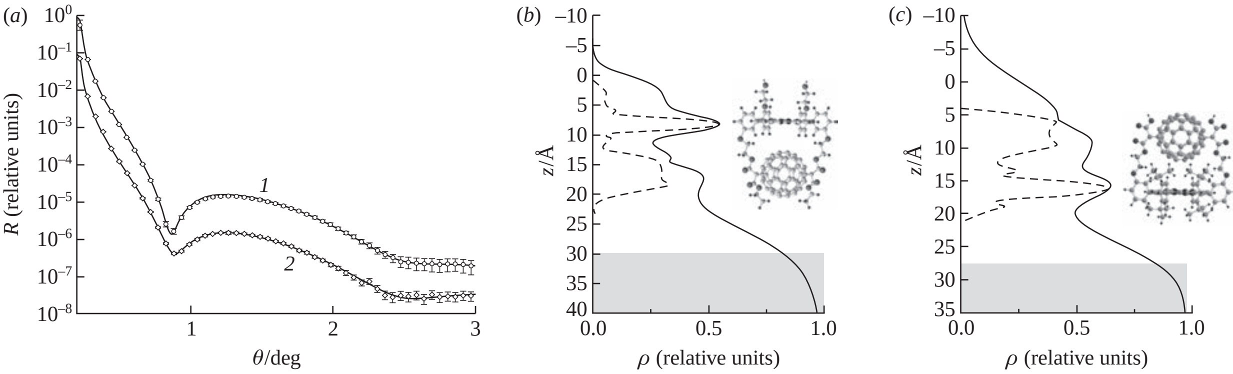


Figure 2 (*a*) The angular dependences of the specular component of the X-ray reflection from (*1*) DHD6ee and (*2*) TBD6a monolayers on a silicon substrate (points, experimental curve; solid line, calculation). (*b*), (*c*) The profiles of the electron density distribution in the depth of DHD6ee and TBD6a monolayers, respectively: solid lines refer to experimental results (received from the X-ray reflectometry curve); dotted lines show theoretical profiles calculated on the basis of molecular modeling. Inserts: (*b*) and (*c*) the models of DHD6ee and TBD6a molecules orientation on a substrate according to electron density profiles, respectively.

were oriented in condensed monolayers on the water subphase surface with porphyrin ring directed towards the liquid. On the solid substrates, the dyad orientation in the films corresponds to the transfer direction (Langmuir–Blodgett and Langmuir–Schaefer films). However, the incorporation of a zinc atom in the dyad affects functional properties. Thus, for the determination of molecular orientation, it is necessary to use the techniques, which would not require modification of the dyad as X-ray reflectivity.[11–13]

The angular dependences of the specular component of the X-ray reflection from DHD6ee and TBD6a monolayer on a silicon substrate[†] are shown in Figure 2(*a*).[‡]

The electron density profiles were found by solving the inverse problem of X-ray reflectivity by an iterative method (nonlinear least-squares fitting).[14] We used the approach based on the representation of the investigated sample as a layered system (the environment, the sub-layers of the film and the substrate), which can be characterized by a stepped profile of the electron density.

For the calculation of a theoretical electron density distribution in the normal direction of the film plane, the 3D models of TBD6a and DHD6ee molecules were constructed taking into account the structural formula, the specific bond lengths and atomic radii and the possible influence of hydrophilic groups on the structure of molecules and area per molecule in monolayer corresponded to the compression isotherms.[15,16] In the packing models the molecules in monolayer were oriented in such a way that their porphyrin rings were parallel to the surface of the subphase (for the DHD6ee dyad porphyrin ring located closer to the subphase, while for the TBD6a dyad fullerene was closer). Theoretical profiles of the electron density in monolayers calculated from the built models were used as a starting approximation in the fitting program.

The theoretical profiles of the electron density distribution in monolayers of DHD6ee and TBD6a obtained from three-dimensional models of molecules were splitted into several sub-layers with a thickness of about 3 Å. Each element of the layered models was given by a set of parameters: thickness, electron density and interface surface. The calculation of the angular dependence of the X-ray reflection specular components was made on the basis of Parratt's recurrence relations.[17] The best fit parameters of the layered system were refined by minimizing the difference between the calculated and experimental data by a nonlinear least-squares method.[14,17]

The values of χ^2 were found to be 1.31 and 1.38 for X-ray reflectometry data for the monolayer of DHD6ee and TBD6a, respectively. In the calculations of chi-square disagreement between the experimental and calculated data starting at 0.4° of the incidence angle were summarized.

The electron density profiles from DHD6ee and TBD6a dyad monolayers are shown in Figure 2(*b*),(*c*). Initial (starting) model dyads orientation in a monolayer did not define the goodness-of-fit criterium, which best value always corresponded to the same electron density distributions [see Figures 2(*b*) and 2(*c*)]. On the profiles, the following peaks can be distinguished: a narrow (relevant to the porphyrin ring) and a broad peak with a lower amplitude (corresponding to the fullerene). The presence of a transition amorphous layer between the solid substrate and the dyad film is due to the technological features of a standard procedure of the solid substrate purification and preparation for the monolayer transfer.

The comparison of the DHD6ee dyad monolayer electron density profile calculated from the experimental curve of X-ray reflectometry with the theoretical profile showed that the molecule (taken into account the roughness) were arranged so that the fullerene moiety was closer to the substrate. A similar comparison of the theoretical and experimental data for the TBD6a dyad monolayer indicates that porphyrin rings of the molecules are directed to the substrate.

Such an arrangement of the dyad monolayers transferred onto solid substrates by the LS method indicates the preferred orientation of the molecules, which is determined by the location of the hydrophilic groups in dyads.

The monolayer thicknesses of DHD6ee and TBD6a obtained from the experimental data of X-ray reflectometry (25 and 22 Å, respectively) are greater than those of the model monolayer (23 and 18 Å, respectively). This can be explained by the presence

---

[†] For the formation of porphyrin–fullerene dyad monolayers and their transfer onto solid substrates, an LB Minitrough system (KSV Instruments) was used. The subphase was a phosphate buffer (0.5 mM Na_2HPO_4 solution and 0.1 mM NaH_2PO_4 solution; pH 7.0) prepared using water of special-purity grade obtained by a Milli-Q purification system (Millipore). During the experiments, the subphase temperature was kept constant (18.0±0.5 °C). The porphyrin–fullerene dyad monolayer was formed on the liquid subphase by spreading the 0.36 mM solution of DHD6ee or TBD6a in chloroform with the subsequent compression at 450 mm^2 min^{-1} using mobile barriers. Formed monolayers were transferred onto solid substrates by the Langmuir–Schaefer (LS) technique at a surface pressure of 15 mN m^{-1}. Silicon wafers were used as substrates. The silicon plates had a polished surface, and they were purified by a standard procedure before use. The transfer ratio coefficient was usually close to unity.

[‡] The X-ray reflectometry measurements were performed on X-ray diffractometers SmartLab, Rigaku (IC RAS) with a rotating Cu anode. A Gebel mirror and a double-crystal Ge-220 monochromator were used for beam monochromatization and collimation. The measurements were carried out with the angular step $\Delta\theta = 0.015°$ and the time per step $t = 6$ s.

of roughness of the substrate, packing defects in the films and a small number of three-dimensional crystallites, the existence of which was shown previously.[10,15,16]

The observed differences in the electron density profiles, namely, less expressed peaks in the case of TBD6a dyad [Figure 2(*c*)] could be due to the differences of dyads interaction with the aqueous subphase in the monolayer. It seems that DHD6ee has more stable position owing to the stronger interaction and, hence, the lower mobility of the porphyrin part of molecule facing to the water than TBD6a dyad that has fullerene in hydrophilic part. This probably results in formation of a significant amount of packing defects in TBD6a monolayer, which leads to a widening of the density profile.

In conclusion, we have demonstrated that the profiles of electron density distributions over the thickness of amphiphilic porphyrin–fullerene dyad monolayers built on the basis of X-ray reflectometry data can be used to determine the presence and degree of preferred orientation of the molecules in the films.

We are grateful to A. V. Efimov (Tampere University of Technology, Finland) for providing us with the materials (TBD6a and DHD6ee dyads).

This study was supported in part by the Russian Foundation for Basic Research (project nos. 14-22-01042_ofi_m and 15-29-01142_ofi_m) and performed using the equipment of the Shared Research Center of IC RAS which was supported by the Ministry of Education and Science of the Russian Federation.

References

1 M. Fujitsuka, H. Shimakoshi, Y. Tei, K. Noda, S. Tojo, Y. Hisaeda and T. Majima, *Phys. Chem. Chem. Phys*., 2013, **15**, 5677.

2 T. Nishizawa, H. K. Lim, K. Tajima and K. Hashimoto, *Chem. Commun.*, 2009, 2469.

3 T. N. Lomova, E. V. Motorina and M. V. Klyuev, *Makrogeterotsikly (Macroheterocycles)*, 2013, **6**, 327 (in Russian).

4 E. S. Zyablikova, N. A. Bragina and A. F. Mironov, *Vestnik MITKhT*, 2012, **7**, no. 5, 28 (in Russian).

5 P. A. Liddell, J. P. Sumida, A. N. Macpherson, L. Noss, G. R. Seely, K. N. Clark, A. L. Moore, T. A. Moore and D. Gust, *Photochem. Photobiol*., 1994, **60**, 537.

6 A. S. Alekseev, N. V. Tkachenko, A. V. Efimov and H. Lemmetyinen, *Russ. J. Phys. Chem. A*, 2010, **84**, 1230 (*Zh. Fiz. Khim*., 2010, **84**, 1356).

7 T. Vuorinen, K. Kaunisto, N. V. Tkachenko, A. Efimov, H. Lemmetyinen, A. S. Alekseev, K. Hosomizu and H. Imahori, *Langmuir*, 2005, **21**, 5383.

8 A. S. Alekseev, H. Lemmetyinen and A. Tolkki, *J. Nanoelectron. Optoelectron.*, 2014, **9**, 741.

9 N. V. Tkachenko, V. Chukharev, P. Kaplas, A. Tolkki, A. Efimov, K. Haring, J. Viheriälä, T. Niemi and H. Lemmetyinen, *Appl. Surf. Sci*., 2010, **256**, 3900.

10 A. Yu. Seregin, Yu. A. D’yakova, S. N. Yakunin, I. A. Makhotkin, A. S. Alekseev, V. V. Klechkovskaya, E. Yu. Tereshchenko, N. V. Tkachenko, H. Lemmetyinen, L. A. Feigin and M. V. Kovalchuk, *Crystallogr. Rep*., 2013, **58**, 937 (*Kristallografiya*, 2013, **58**, 937).

11 K. N. Stoev and K. Sakurai, *Spectrochim. Acta, Part B*, 1999, **54**, 41.

12 C. Stefaniu and G. Brezesinski, *Curr. Opin. Colloid Interface Sci*., 2014, **19**, 216.

13 O. V. Konovalov and L. A. Feigin, *J. Phys. IV*, 1993, **3**, 185.

14 J. S. Pedersen and I. W. Hamley, *J. Appl. Crystallogr*., 1994, **27**, 36.

15 Yu. A. D’yakova, E. I. Suvorova, A. S. Orekhov, A. S. Alekseev, V. V. Klechkovskaya, E. Yu. Tereshchenko, N. V. Tkachenko, H. Lemmetyinen, L. A. Feigin and M. V. Kovalchuk, *Crystallogr. Rep*., 2011, **56**, 157 (*Kristallografiya*, 2011, **56**, 163).

16 Yu. A. D’yakova, E. I. Suvorova, Andrei S. Orekhov, Anton S. Orekhov, A. S. Alekseev, R. V. Gainutdinov, V. V. Klechkovskaya, E. Yu. Tereshchenko, N. V. Tkachenko, H. Lemmetyinen, L. A. Feigin and M. V. Kovalchuk, *Crystallogr. Rep*., 2013, **58**, 927 (*Kristallografiya*, 2013, **58**, 930).

17 L. G. Parratt, *Phys. Rev.*, 1954, **95**, 359.

Received: 24th November 2015; Com. 15/4781