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Supramolecular self-assembly study of a flexible perylenetetracarboxylic diimide dimer in Langmuir and Langmuir–Blodgett films

Yanli Chen [a,*], Ye Kong [a], Yanfeng Wang [b], Pan Ma [b], Meng Bao [a], Xiyou Li [b,*]

[a] *College of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, China*
[b] *Department of Chemistry, Shandong University, Jinan 250100, China*

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ABSTRACT

A novel perylenetetracarboxylic diimide molecule (**2PDI-TAZ**), which contains two perylenetetracarboxylic diimide (PDI) attached to a melamine headgroup, was designed and synthesized. Supramolecular self-assemblies were studied in Langmuir and Langmuir–Blodgett films. Surface pressure–area isotherm measurements and the spectroscopic studies indicate that the **2PDI-TAZ** molecules adopted a face-to-face configuration and edge-on orientation in Langmuir or the multilayer LB films. The presence of the barbituric acid in subphase change the hydrophilicity of **2PDI-TAZ** due to the hydrogen bonding between melamine and barbituric acid, which has been revealed by the π–A isotherms and the FT-IR spectra. Transmission electron microscopy images of the LB films deposited from the barbituric acid solution revealed uniform nanowire morphology while the X-ray diffraction studies indicate that the molecules in the solid film packed with high order. The strong excimer emission of **2PDI-TAZ** in LB films suggests enforced face-to-face configuration for the PDI unites in LB films in relative to that in solution.

1. Introduction

Perylenetetracarboxylic diimide (PDI) organic derivatives represent an extremely important class of molecules with promising application potentials in many areas of scientific research [1]. The unique properties of PDIs, such as strong absorption and emission, good semi-conductivity, excellent thermal and chemical stabilities, have attracted extensive interest in the applications in photovoltaic cells [2–7], chemical sensors [8–11], electroluminescent devices [12–15], and organic field effect transistors (OFETs) [16–19]. The orderness of PDI molecules in the device has been proved to be crucial for the device performance. For example, increasing the ordering of perylene molecules could promote the charge transfer and thus improve the efficiency of the solar cells [4,20,21], the performance of an OFET could be promoted by changing the packing model of organic molecules in the solid films [22–24]. Therefore, the development of novel fabrication methods for the highly ordered PDI film is important and is now one of the most active fields in the area of molecular electronics.

Langmuir and Langmuir–Blodgett (LB) techniques are useful tools to fabricate monolayer and/or multilayer films with controllable structure in the molecular level [25]. However, the application of LB techniques in the construction of PDI films are scarcely reported so far probably because of the difficulties on the synthesis of amphiphilic PDIs. On the other hand, the supramolecular approach to the ordered PDI assembly based on various non-covalent interactions such as π–π interaction, van der Waals forces, hydrogen bonding, static electronic interactions, and metal-ligand coordinations, have attracted a lot of interest in the past decade [26]. A significant amount of work has been reported on the study of perylene assemblies for artificial photosynthesis and molecular photonic/electronic material development through the supramolecular chemistry approach [27,28].

Combination of supramolecular interactions with the LB technique to develop highly ordered and well-defined thin solid film is an important development of the LB film fabrication. We are particularly interested in a supramolecular self-assembly system formed from complementary hydrogen bonding between barbituric acid and melamine. Melamine has a structural triad of hydrogen-bonding donor–acceptor–donor, while barbituric acid has a complementary motif of hydrogen-bonding acceptor–donor–acceptor. When these two compounds are mixed together, highly ordered supramolecular network structures such as linear tapes, crinkled tapes, and rosettes can be formed in solid state or solution [29,30]. This supramolecular system was also studied at the air–water interface. In contrast to the traditional belief that hydrogen bonding is not so efficient in aqueous solution, studies by a few research groups demonstrated that a highly ordered and rigid linear network was formed between amphiphilic barbituric acid and melamine with its complementary components in Langmuir and

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[*] Corresponding authors.
E-mail address: chm_chenyl@ujn.edu.cn (Y. Chen).

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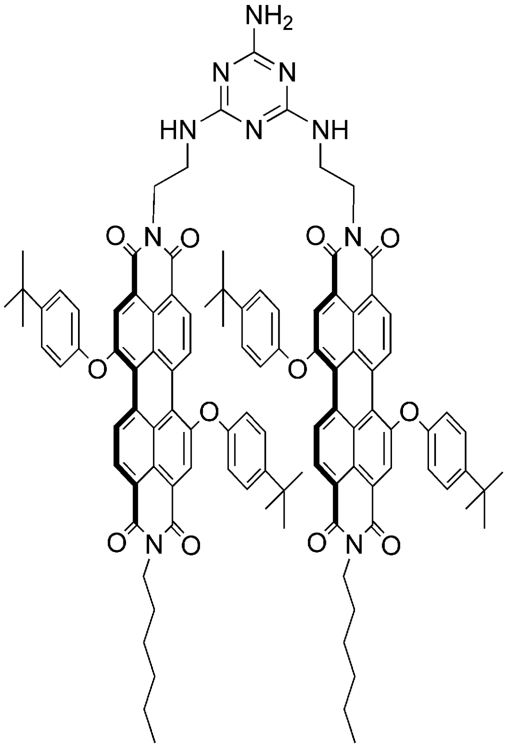

Fig. 1. Molecular structure of **2PDI-TAZ**.

Langmuir–Blodgett films [31–34]. Moreover, it was reported by Huo et al. that such a linear hydrogen bonding network could have a dramatic effect on the photopolymerization of a diacetylene monolayer film and the properties of the resulting polydiacetylene film [35,36].

In order to achieve a PDI thin solid film with high ordered structure, the combination of hydrogen bonding with LB techniques is a rational design. In the present paper, we report the design, synthesis, of a novel PDI compound with phenoxy groups at the bay positions and hydrophobic alkyl substituents at the two imide nitrogens of the PDI molecule. Specifically, two of these PDI moieties were linked by a hydrophilic melamine ring to form a flexible PDI double-decker dimer, **2PDI-TAZ**, Fig. 1. The resulting **2PDI-TAZ** molecule maintains the melamine structural motif of two-face hydrogen-bonding donor–acceptor–donor and is expected to form a linear supramolecular self-assembly with barbituric acid at the air–water interface. This hydrogen bonding together with the π–π interactions between the PDI rings and the hydrophobic/hydrophilic interactions are expected to drive the molecules to form a highly ordered structure. Herein we report the results.

2. Materials and methods

2.1. General remarks

Surface pressure–area (π–A) isotherms were recorded on a NIMA Langmuir–Blodgett 2000 trough (NIMA technology, UK). Electronic absorption spectra were recorded on a Hitachi U-4100 spectrophotometer while the fluorescence spectra and the lifetimes were measured on a ISIS K2 system (USA). FT-IR spectra were recorded on a BIORAD FTS-165 spectrometer (Perkin–Elmer Ltd, USA) with a resolution of 2 cm^{-1}. Low angle X-ray diffraction (LAXRD) experiments were carried out on a Rigaku D/max-γB X-ray diffraction system. The TEM images were taken on a H600 electron microscope operated at 100 kV (Hitachi, Japan).

2.2. Surface pressure–area isotherm measurement

The surface pressure was measured using the Wilhelmy plate method with the accuracy of ±0.1 mN/m. HPLC grade dichloromethane was used to prepare the **2PDI-TAZ** solution for Langmuir monolayer study. For the spreading solution, **2PDI-TAZ** was dissolved in dichloromethane to a concentration of 1.91×10^{-4} mol/L. The Langmuir monolayer study was conducted at an ambient temperature of $25 \pm 2\,^{\circ}\mathrm{C}$. The π–A isotherms were recorded 15 min after spreading the dichloromethane solutions onto the surface of pure water (resistivity: 18 MΩ/cm, pH 6.4) or 1 mM barbituric acid aqueous solution with a compression rate of 20 cm^2/min. All the isotherms were repeated more than three times, and the deviation between any of the three individual isotherms is within ±0.02 nm^2/molecule.

2.3. Thin film deposition and characterization

All LB films for low-angle X-ray diffraction, UV–vis, polarized UV–vis, fluorescence, and FT-IR spectra measurement were deposited onto hydrophobic quartz plates or $\mathrm{CaF_2}$ substrates by vertical dipping method with a dipping speed of 7 mm/min while the surface pressure was kept at 25 mN/m. The time interval between two consecutive layer depositions was 15 min. Because of the good amphiphilic properties of **2PDI-TAZ**, the transfer ratio during the film deposition for both of the subphases is close to unity, indicating a very good layered structure for the LB films, Figs. S1 and S2 (supplementary material). For the polarized spectra, a dichroic sheet polarizer was placed in front of the LB films with s- and p-polarized lights, respectively. Literature method described by Hönig et al. was adopted to treat the substrates [37]. The Langmuir film for TEM characterization was deposited onto the copper grids using subphase lowering method. The samples have been dried in air for ca. 12 h at room temperature before being loaded into the vacuum chamber of the electron microscope.

3. Results and discussion

3.1. Molecular design and synthesis

This **2PDI-TAZ** was designed with the idea of increasing the face-to-face interactions of neighboring PDIs in mind since many examples have revealed that large face-to-face interaction between neighboring molecules are beneficial to the performance of photonic and electronic device [38–42]. The linkage, melamine ring, used to connect two monomeric PDIs units, is well known for its hydrogen bonding with barbituric acid and forming face-to-face conformation for the connected two chromophores [43–46] and therefore provides possibility for ordering the molecules in solid film through hydrogen bonding [33,34,47,48]. The detailed synthetic procedures together with the structure characterization are described in supplementary material. **2PDI-TAZ** shows very good solubility in organic solvents, which renders it possible to fabricate this compound into highly ordered film structures through solvent-based procedure especially by LB technique due to the typical amphiphilic nature.

3.2. Characteristics of pressure–area isotherms

Reproducible pressure–surface area (π–A) isotherms for **2PDI-TAZ** on the surface of pure water and 1 mM barbituric acid subphase indicate that the compound can form stable monolayer on both subphases, Fig. 2. As illustrated in this figure, monolayer of **2PDI-TAZ** formed on the surface of both pure water and barbituric acid solution show similar interface behavior. For example, the π–A isotherm of **2PDI-TAZ** shows a liquid condensed phase

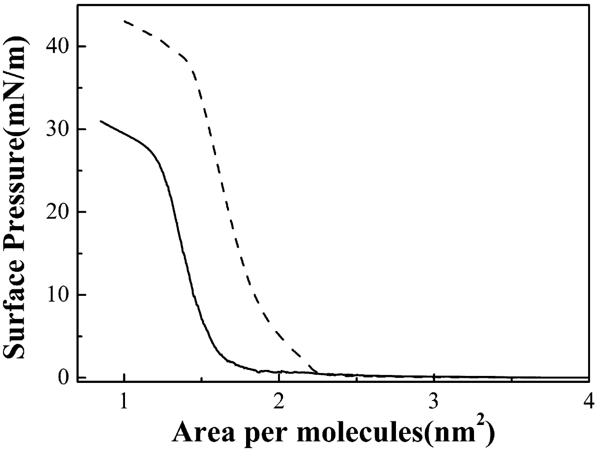

Fig. 2. π–A isotherms of **2PDI-TAZ** on the surface of water (solid) and 1 mM barbituric acid solution (dash).

between surface pressure of 1 and 8 mN/m and a solid phase between 8 and 26 mN/m on pure water subphase, while the corresponding phase appears at 0.8–16 mN/m and 16–38 mN/m respectively on barbituric acid subphase. The collapse point, which is the phase change observed when the value $d\pi/dA$ decreases, gives the collapse pressure at ∼26 and ∼38 mN/m on pure water and barbituric acid solution, respectively. Higher collapse pressure on barbituric acid solution for monolayer of **2PDI-TAZ** exhibited greater stability and the better film forming ability than that on pure water subphase, which implied anchoring effect of barbituric acid and improved molecular orientation in the monolayer [49].

The limiting mean molecular occupied area, which is estimated by extrapolating the steeply rising part of the π–A isotherm curve to zero pressure, is 1.60 nm^2/molecule on pure water subphase, which is slight bigger than that of the projection for a perpendicular standing molecule of **2PDI-TAZ** estimated from the minimized structure, 1.10 nm^2/molecule, but much smaller than a molecular planar area with a monomeric PDI moiety facing on water surface, 6.14 nm^2/molecule [19,50,51]. Edge-on with hydrophilic melamine ring staying close to the water surface and the hydrophobic perylene cores obliged towards the air phase would be the most possible orientation for molecules of **2PDI-TAZ**. On the surface of barbituric acid solution, the π–A isotherm of **2PDI-TAZ** gives a limiting molecular area of 1.95 nm^2/molecule, which is a little bit larger than that on the water surface. Taking into account the limited cross section of a barbituric acid molecule (∼0.36 nm^2/molecule) [34], such a molecular area expansion relative to that on water surface clearly indicates the binding of barbituric acid to the monolayer, as also shown in many previous studies on this supramolecular system [52,53]. Hydrogen bonding network between melamine ring and barbituric acid should be formed, Fig. 3.

3.3. Morphologies of the Langmuir film

To investigate the morphology of the film using TEM technique, the Langmuir monolayer films of **2PDI-TAZ** formed on the two different subphases were deposited onto Formvar-coated 230 mesh copper grids by subphase lowering method.

As shown in Fig. 4A, the favorable π–π stacking between the PDI unites of **2PDI-TAZ** leads to the formation of the nanofibers in the monolayer film deposited from the surface of water. The morphology of the monolayer film deposited from the surface of barbituric acid solution reveal nanowires with large aspect ratio, Fig. 4B. The nanowires thus obtained show quite uniform morphology with the average width of ca. 150 nm, and the length of tens of micrometers. It is worth noting that the morphology of monolayers is not homogeneous due to self-aggregation of the molecules in Langmuir film. The similar monolayer behaviors were also observed with amphiphilic and nonamphiphilic materials such as the monolayers of pure (Pc)Dy[Pc(OC$_n$H$_{2n+1}$)$_8$]Dy(Pc) film [54], a phthalocyanine (Pc) modified with eight benzyloxyethoxy groups (CuPc(OC$_2$OBz)$_8$ and H$_2$Pc(OC$_2$OBz)$_8$) [55], the liquid crystalline perylenetetracarboxylic diimide derivative, N,N'-bis[3-[2-[2-[2-(2-cyanoethoxy)ethoxy]ethoxy]ethoxy]-propyl]-perylene-3,4:9,10-tetracarboxyldiimide [56] and monolayers of 5,10,15,20-tetra-4-oxy(acetic acid)phenylporphyrin [57]. These nanomaterials are highly desired for fabricating nanowire-based optoelectronic devices which often require a wide variety of channel lengths to achieve the optimum gate or optical modulation [58].

3.4. FT-IR spectra

The infrared spectra for **2PDI-TAZ** dispersed in KBr and its LB films deposited from both subphases are shown in Fig. 5. In line with that of perylene analogous [59–61], the principal in-plane bands at 1660 and 1698 cm^{-1} correspond to the O=CN stretches while the in-plane bands at 1596 and 1572 cm^{-1} correspond to the C=C aromatic stretches. The principal out-of-plane band is at 812 cm^{-1} and has been assigned as the wagging modes of C–H on perylene ring. The out-of-plane wagging vibrations of the perylene ring provide a dynamic dipole perpendicular to that of the O=CN or C=C stretching vibrations. All of these bands were observed in the reference spectrum of unoriented **2PDI-TAZ** in KBr pellets, Fig. 5a. Changes in the relative intensities of the in-plane modes or the out-of-plane modes in LB films with respect to those

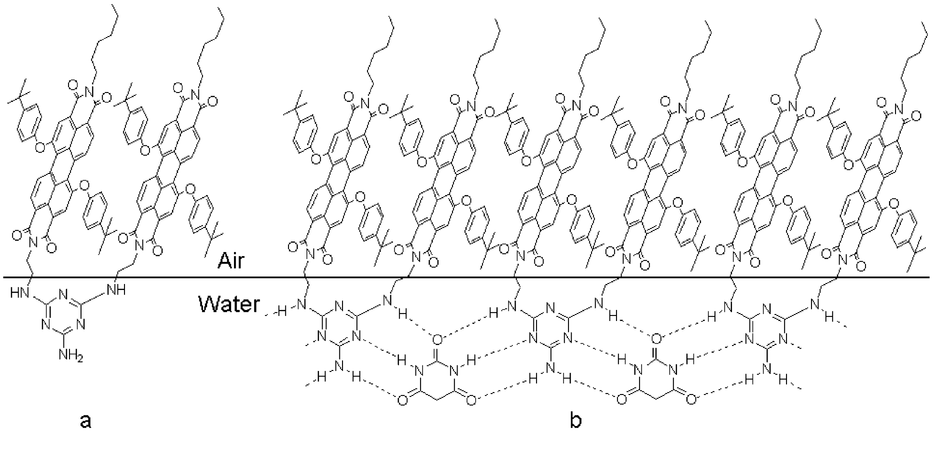

Fig. 3. Schematic arrangement of **2PDI-TAZ** on the surface of water (a) and 1 mM barbituric acid solution (b).

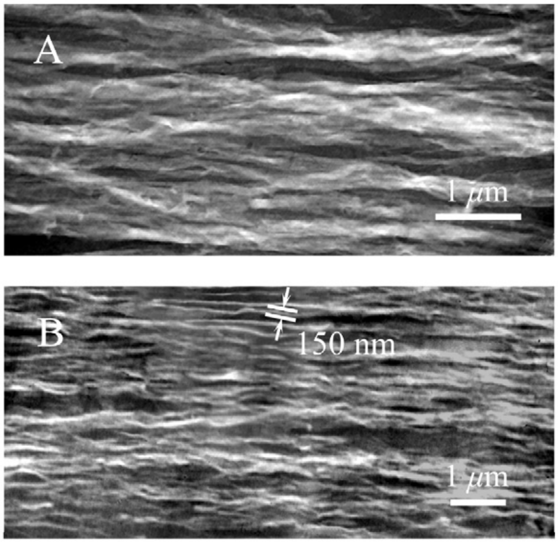

Fig. 4. TEM images of **2PDI-TAZ** Langmuir film formed on the surface of pure water (A) and 1 mM barbituric acid solution (B).

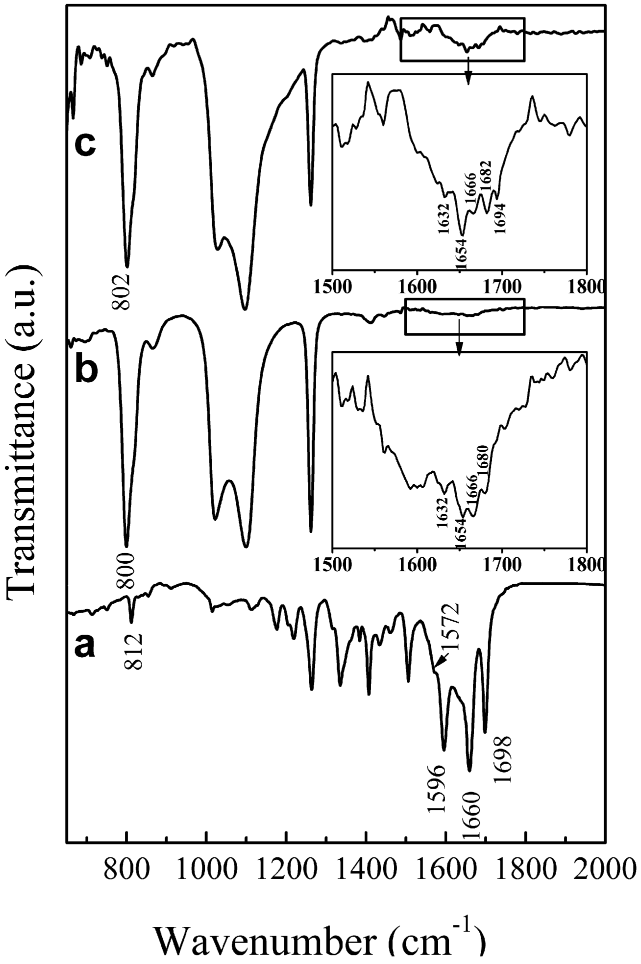

Fig. 5. FT-IR spectrum of **2PDI-TAZ** dispersed into a KBr pellet (a), ATR-IR spectra of **2PDI-TAZ** LB films deposited from pure water (b), and from 1 mM barbituric acid solution (c).

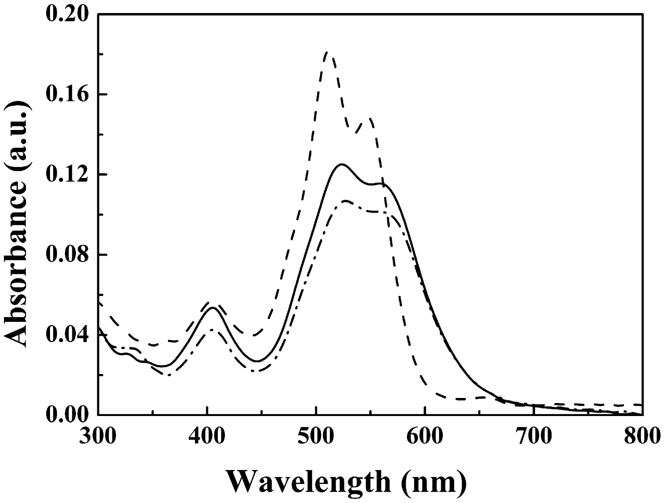

Fig. 6. Absorption spectra of **2PDI-TAZ** in dichloromethane (dash line) and 10-layer LB films (solid line, from water surface; dash dot line, from 1 mM barbituric acid solution).

of **2PDI-TAZ** in KBr pellets yield information concerning the orientation of the molecules in the films [62]. For transmission, the polarization of the incident radiation always lies along the substrate surface. Therefore, only bands with a change in dipole moment parallel to the substrate surface will be intensified while the bands perpendicular to the substrate surface will be comparatively weak. The wagging vibration is the most intense band in the IR spectrum of the LB films as shown in Fig. 5, b and c, while the in-plane vibrations are broad and very weak. Since the intensity is proportional to the dot product of the electric field and the dynamic dipole, the average PDI plane of **2PDI-TAZ** should perpendicular to the substrate surface, suggesting an edge-on orientation for the molecules in LB films. This is in line with the results of π–A isotherms. Similar result for the solid film of 3,4,9,10-perylenetetracarboxylic diimide derivatives are also reported by Tam-Chang and co-workers [61].

Comparing with the IR spectra of **2PDI-TAZ** LB films deposited from pure water (inset of Fig. 5b), the spectrum of the LB films deposited from the surface of 1 mM barbituric acid aqueous solution (inset of Fig. 5c) clearly reveal the formation of hydrogen-bonds. A strong C=O peak of bound barbituric acid is observed at 1694 cm^{-1} in Fig. 5c, which is absent in Fig. 5b. As reported previously, the C=O peak of barbituric acid in an argon matrix appears at 1754 (for the monomer) and 1732 (for the dimer) cm^{-1}, but these peaks shift to 1694 cm^{-1} in the solid state at 20 K, owing to hydrogen-bond formation between molecules of barbituric acid [63].

3.5. UV–vis absorption spectra

The absorption spectra of **2PDI-TAZ** in solution, LB films deposited on quartz from the surface of water or barbituric acid solution are shown in Fig. 6. The absorption spectra of PDI derivatives containing one or two perylene chromophores usually consist of one electronic transition with a characteristic vibronic structure [64]. The spectrum of **2PDI-TAZ** in solution has a characteristic vibronic structure associated with the π–π^* electronic transitions of PDI chromophores with a 0–0 band at 547 nm followed by subsequent transitions 0–1 at 512 nm and 0–2 at 405 nm. This absorption spectrum corresponds well to many other folded and circular perylene dimers reported previously [19,65,66]. The intensity of the vibrational transitions within the progression follows the order 0–1 > 0–0, which is commonly attributed to the intramolecular π–π stacking in PDI dimer [65,66].

In the spectrum of the LB films deposited from the water surface or barbituric acid subphase, obvious band broadening was observed, which could be ascribed to the field effects of the closely compacted molecular assembly. The main 0–1 transition

Table 1
The orientation angles of the PDI ring of **2PDI-TAZ** in the LB films deposited from the surface of water and 1 mM barbituric acid solution.

	$A_{\parallel}$	$A_{\perp}$	D_0 ($A_{\parallel}/A_{\perp}$)	$A_{\parallel}$	$A_{\perp}$	D_{45} ($A_{\parallel}/A_{\perp}$)	θ
A—10 layers (520 nm)[a]	0.07371	0.09265	0.7956	0.09926	0.1182	0.8398	53.63°
B—10 layers (523 nm)[b]	0.09775	0.1021	0.9574	0.1136	0.1198	0.9482	56.02°

[a] A = LB films of **2PDI-TAZ** deposited from pure water subphase.
[b] B = LB films of **2PDI-TAZ** deposited from 1 mM barbituric acid subphase.

appears at 524 and 527 nm, while the 0–0 vibronic progression is found at 559 and 563 nm in **2PDI-TAZ** LB films from pure water and barbituric acid solution, respectively. Compared to that of dichloromethane solution, these absorptions are red-sifted, which has also reported previously for the LB films of other PDIs [67–69]. The red shift of the main absorption bands has been attributed to two possible reasons: one is related to an edge-to-edge (J-type) aggregation of the PDI molecules in the monolayer film, and the other is attributed to conformational change of the PDI macrocycle from nonplanar structures in solution to planar structures in solid films. Judging from the limiting molecular area of the **2PDI-TAZ** on the surface of both water and barbituric acid subphase, it is unlikely that the PDIs formed J-aggregates within the monolayer film. It is more reasonable to attribute the red shift of the main absorption bands to a greater π-electron delocalization in the film than in solution because of the more planar conformation of the macrocycle in the film. The absorption spectra of the LB films deposited from the surface of water or barbituric acid solution do not show large difference, suggesting similar packing model for PDI molecules in the LB films with or without barbituric acid.

The linear relationship between the layer number and the absorbance at 524 or 527 nm of **2PDI-TAZ** LB films from both pure water and barbituric acid solution was obtained, Figs. S3 and S4. The fact suggests that the monolayer at air/water interface would be transferred uniformly onto the substrate and the microscopic environment of **2PDI-TAZ** molecules remains unchanged with the layer number.

3.6. Orientation of PDI ring in the transferred LB films

Polarized UV–vis absorbance of LB films has been widely used in determining the orientation of a planar chromophore in LB films previously. When the polarized direction of light is parallel to the direction of the excitation dipole moment of the molecule, an intense absorbance could be observed. Otherwise, a weak absorbance would be recorded. The polarized electronic absorption spectra of **2PDI-TAZ** on quartz deposited from pure water and barbituric acid solution are shown in Fig. 7. An obvious dichroism at incidence angles of both 0° and 45° was observed, implying the alignment or anisotropy of the LB films in relation to deposition plane. Assuming that the π–π^* transition dipoles of the 0-1 band are uniformly distributed in the PDI ring plane [61,68], the relative exact orientation angle (θ) between the PDI plane and the substrate surface normal can be calculated by the method of Yoneyama [70]. The experimental results and the calculated θ are summarized in Table 1. The tilt angles of the PDI rings in the films deposited from either pure water or barbituric acid solution are both around 55°, supporting the edge-on configuration as revealed by the π–A isotherms and the IR studies. The little bit larger title angle presented by the films deposited from the surface of barbituric acid solution relative to that deposited from water surface might be attributed to the enforced hydrophilic property due to the formation of hydrogen bonding between barbituric acid and melamine headgroup. The enforced hydrophilic property will keep the molecule close to the water surface while the repulsion from aqueous subphase surface associated with hydrophobic PDI groups with long alkyl side chains push the whole molecule away, and these two contrary interactions force the molecules to adapt a more titled orientation on the surface of barbituric acid solution.

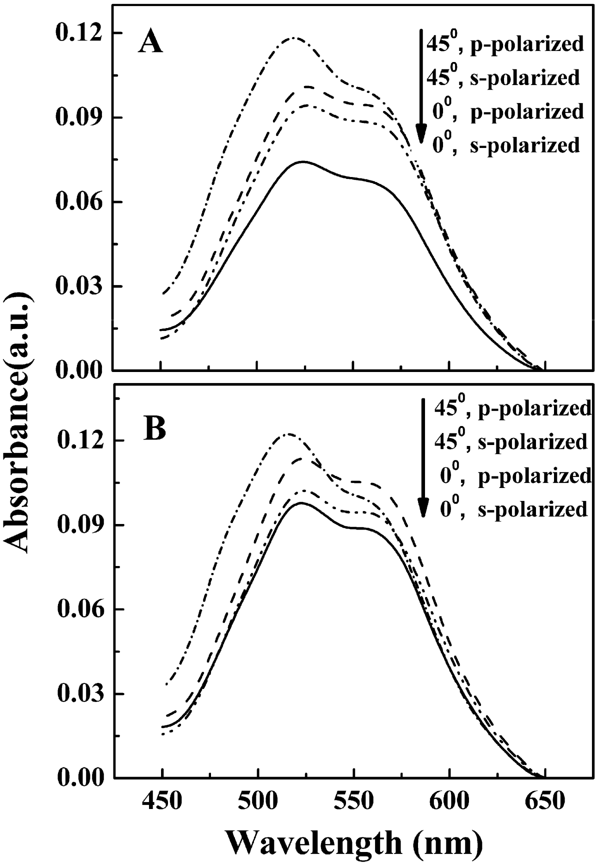

Fig. 7. Polarized UV–vis absorption spectra of the LB films of **2PDI-TAZ** deposited from the surface of water (A) and 1 mM barbituric acid solution (B).

3.7. Low-angle X-ray diffraction

The quality of deposited LB films of **2PDI-TAZ** has been further assessed using a low-angle X-ray diffraction (LAXRD) technique. The LB films of **2PDI-TAZ** deposited from the surface of water or barbituric acid solution give clear diffraction peaks in their low angle region, Fig. 8. The existence of only a single diffraction peak with its higher order diffractions indicates that the films are highly ordered in a layered structure [71]. As shown in Fig. 8A, in the **2PDI-TAZ** LB films deposited from the surface of water, two diffraction peaks at $2\theta = 2.48$ and 4.95° are the first- and second-order diffractions corresponding to a spacing of 3.57 nm. As the LB films of **2PDI-TAZ** are Y type LB film, therefore the thickness of monolayer is 1.79 nm, which is significantly smaller than the length of the molecule of **2PDI-TAZ**. Comparison between these experimental results and the dimension of the molecules leads to such a conclusion that the molecules are packing with the molecular

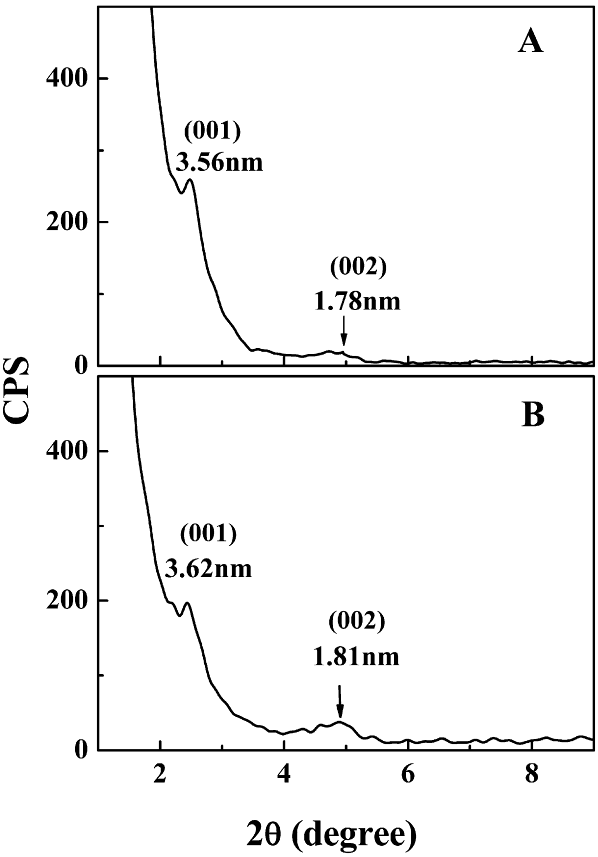

Fig. 8. Low angle X-ray diffraction patterns for the LB films of **2PDI-TAZ** deposited from the surface of water (A) and 1 mM barbituric acid solution (B).

plane titled with respect to the substrate. The hydrophobic flexible alkyl side-chains maybe tilted, folded, or interpenetrated in the film as reported previously for other PDI films [58,72].

The LB films of **2PDI-TAZ** deposited from the surface of barbituric acid solution give similar LAXD diffraction patterns, indicating similar layered structure and similar orientations of molecules in solid film. This finding is in line with that deduced from the π–A isotherm, UV–vis absorption, and polarized electronic absorption spectroscopic studies. However, the thickness of the monolayer calculated from the 2θ value (1.81 nm) is a little bit larger than that found for the LB films deposited from water surface. This might be ascribed to the complementary hydrogen bonding between barbituric acid and melamine headgroup from **2PDI-TAZ** which drive the PDI rings take a more titled orientation as revealed by the polarized absorption spectra.

3.8. Fluorescence spectra

PDI is a kind of excellent fluorescent compound with fluorescence quantum yield as high as 100% [73]. Their fluorescence spectra are sensitive to the molecular structure as well as the environment, therefore they are useful tools for the investigation of the structure of PDI thin solid films [19,74]. According to the previous research, a broad and weak excimer's emission at longer wavelength is expected for **2PDI-TAZ** in solution [19]. However, the fluorescence spectrum of **2PDI-TAZ** in solution presents one strong emission band at 578 nm with a shoulder at 626 nm (Fig. 9), a typical emission of monomeric PDI [75]. But the fluorescence quantum yield calculated for **2PDI-TAZ** in CH_2Cl_2 solution is only 10%, which is remarkably smaller than that of monomeric PDIs. We ascribed the emission of **2PDI-TAZ** in solution to a mixture of the emission from monomeric PDI and excimer. The monomeric emission comes from trace of non face-to-face stacked **2PDI-TAZ** in solution and the excimer's emission has been overlapped with the monomeric PDI's emission. This has been further supported by the fluorescence lifetime measurements. Two fluorescence lifetimes were detected for **2PDI-TAZ** in solution with the short one (3.73 ns) corresponding to the monomeric PDI's emission while the longer one (13.6 ns) corresponding to the excimer's emission [76]. These results suggest an equilibrium between the face-to-face stacked configuration and non face-to-face stacked configuration for **2PDI-TAZ** in solution with the former as the dominate species. The fluorescence spectra of **2PDI-TAZ** in LB films are shown in Fig. 10. No emission of the monomeric PDI was observed in these spectra, implying that all the molecules were assembled into face-to-face stacked aggregate [58,74].

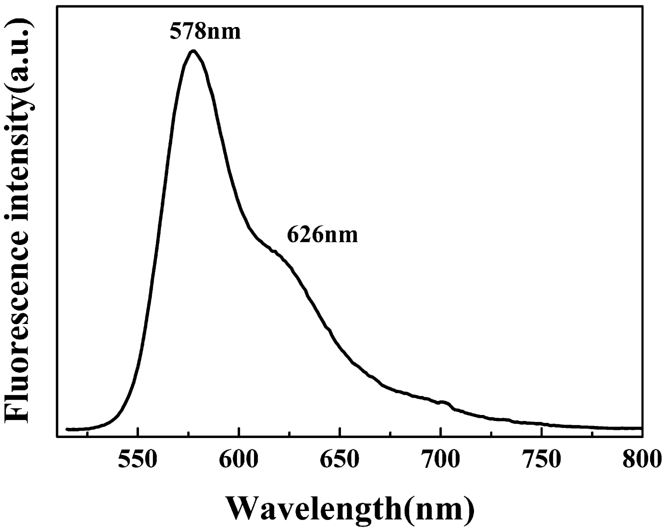

Fig. 9. Fluorescence spectra of **2PDI-TAZ** in dichloromethane (excitation at 500 nm).

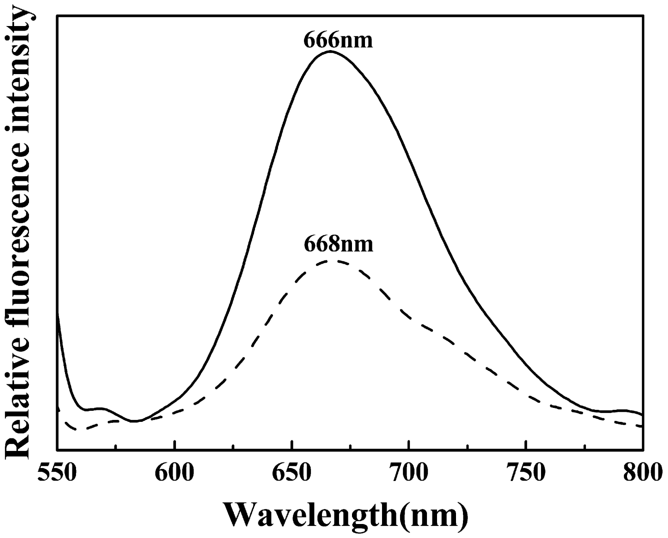

Fig. 10. Fluorescence spectra of 10-layer **2PDI-TAZ** LB films deposited from pure water (solid) and 1 mM barbituric acid subphase (dash) (excitation at 500 nm).

4. Summary

The **2PDI-TAZ** molecule containing two perylenetetracarboxylic diimide and a melamine headgroup has very good amphiphilic properties and can form very stable monolayer on the surface of water and barbituric acid aqueous solution. The monolayer can be transferred to the substrate by vertical dipping method to form multilayer LB films with highly ordered structure. The barbituric acid in subphase can form hydrogen bonding with melamine, which can enforce the hydrophilicity of **2PDI-TAZ** and tune the orientation of the molecules in solid films a little bit. The uniform nanowires formed on the surface of both water and barbituric acid solution driven by the strong π–π interactions as well as hydrogen bondings were expected to offer an alternate approach in refining the properties of the PDI materials.

High ordered organic semiconductor nanostructures provide enormous prospective applications in optoelectronic devices. The two kinds of LB films fabricated in this study are currently being employed in the application studies involving both electrical and optical properties. For example, the strong π–π stacking and the long-range molecular organization would provide the resulted LB films with feasibly detectable conductivity, which in turn is expected to be dependent on the local electrical field due to the modulation on the π-electron delocalization. Such properties will enable us to fabricate new types of field effect transistors and gas sensors.

Acknowledgments

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Supplementary material

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References

[1] K.-Y. Law, Chem. Rev. 93 (1993) 449.
[2] L. Schmidt-Mende, A. Fechtenkotter, K. Müllen, E. Moons, R.H. Friend, J.D. MacKenzie, Science 293 (2001) 1119.
[3] B.A. Gregg, J. Phys. Chem. B 107 (2003) 4688.
[4] B.A. Gregg, J. Phys. Chem. 100 (1996) 852.
[5] G. Tamizhmani, J.P. Dodelet, R. Cote, D. Gravel, Chem. Mater. 3 (1991) 1046.
[6] Y. Liu, S. Xiao, H. Li, F. Lu, J. Zhuang, D. Zhu, J. Phys. Chem. B 108 (2004) 6256.
[7] E. Peeters, P.A. Van Hal, S.C.J. Meskers, R.A.J. Janssen, E.W. Meijer, Chem. Eur. J. 8 (2002) 4470.
[8] R. Liu, M.W. Holman, L. Zang, D.M. Adams, J. Phys. Chem. A 107 (2003) 6522.
[9] M.W. Holman, R. Liu, L. Zang, P. Yan, S.A. DiBenedetto, R.D. Bowers, D.M. Adams, J. Am. Chem. Soc. 126 (2004) 16126.
[10] M. Sauer, Angew. Chem. Int. Ed. 42 (2003) 1790.
[11] C. Grimsdale, K. Mullen, Angew. Chem. Int. Ed. 44 (2005) 5592.
[12] D. Gosztola, M.P. Niemczyk, W. Svec, A.S. Lukas, M.R. Wasielewski, J. Phys. Chem. A 104 (2000) 6545.
[13] M.A. Angadi, D. Gosztola, M.R. Wasielewski, J. Appl. Phys. 83 (1998) 6187.
[14] S. Alibert-Fouet, S. Dardel, H. Bock, M. Oukachmih, S. Archambeau, I. Seguy, P. Jolinat, P. Destruel, Chem. Phys. Chem. 4 (2003) 983.
[15] P. Ranke, I. Bleyl, J. Simmerer, D. Haarer, A. Bacher, H.W. Schmidt, Appl. Phys. Lett. 71 (1997) 1332.
[16] J. Locklin, D. Li, S.C.B. Mannsfeld, E.-J. Borkent, H. Meng, R. Advincula, Z. Bao, Chem. Mater. 17 (2005) 3366.
[17] C.W. Struijk, A.B. Sieval, J.E.J. Dakhorst, M. Dijk, P. Kimkes, R.B.M. Koehorst, H. Donker, T.J. Schaafsma, S.J. Picken, A.M. Van de Craats, J.M. Warman, H. Zuilhof, E.J.R. Sudhölter, J. Am. Chem. Soc. 122 (2000) 11057.
[18] Z. Chen, M.G. Debije, T. Debaerdemaeker, P. Osswald, F. Würthner, ChemPhysChem 5 (2004) 137.
[19] Y. Wang, Y. Chen, R. Li, S. Wang, W. Su, P. Ma, M.R. Wasielewski, X. Li, J. Jiang, Langmuir 23 (2007) 5936.
[20] P.M. Kazmaier, R. Hoffmann, J. Am. Chem. Soc. 116 (1994) 9684.
[21] B.A. Gregg, J. Sprague, M.W. Peterson, J. Phys. Chem. B 101 (1997) 5362.
[22] C.D. Dimitrakopoulos, A.R. Brown, A. Pomp, J. Appl. Phys. 80 (1996) 2501.
[23] C.D. Dimitrakopoulos, D.J. Mascaro, IBM J. Res. Dev. 45 (2001) 11.
[24] K. Xiao, Y.Q. Liu, G. Yu, D.B. Zhu, Appl. Phys. A 77 (2003) 367.
[25] M.C. Petty, Langmuir–Blodgett Films: An Introduction, Cambridge Univ. Press, Cambridge, 1996.
[26] A.A. Johannes, W. Elemans, R. van Hameren, R.J.M. Nolte, A.E. Rowan, Adv. Mater. 18 (2006) 1251.
[27] A. Syamakumari, A.P.H.J. Schenning, E.W. Meijer, Chem. Eur. J. 8 (2002) 3353.
[28] A.P.H.J. Schenning, J. van Herrikhuyzen, P. Jonkheijm, Z. Chen, F. Würthner, E.W. Meijer, J. Am. Chem. Soc. 124 (2002) 10252.
[29] J.A. Zerkowski, C.T. Seto, D.A. Weirda, G.M. Whitesides, J. Am. Chem. Soc. 112 (1990) 9025.
[30] J.A. Zerkowski, J.P. Mathias, G.M. Whitesides, J. Am. Chem. Soc. 116 (1994) 4305.
[31] M. Weck, R. Fink, H. Ringsdorf, Langmuir 13 (1997) 3515.
[32] H. Koyano, P. Bissel, K. Yoshihara, K. Ariga, T. Kunitake, Chem. Eur. J. 3 (1997) 1077.
[33] Q. Huo, L. Dziri, B. Desbat, K.C. Russell, R.M. Leblanc, J. Phys. Chem. B 103 (1999) 2929.
[34] T. Hasegawa, Y. Hatada, J. Nishijo, J. Umemura, Q. Huo, R.M. Leblanc, J. Phys. Chem. B 103 (1999) 7505.
[35] Q. Huo, R. Stoyan, T. Hasegawa, J. Nishijo, J. Umemura, G. Puccetti, K.C. Russell, R.M. Leblanc, J. Am. Chem. Soc. 122 (2000) 7890.
[36] Q. Huo, S. Wang, A. Pisseloup, D. Verma, R.M. Leblanc, Chem. Commun. (1999) 1601.
[37] E.P. Hönig, J.H.T. Hengst, D.D. Engelsen, J. Colloid Interface Sci. 45 (1973) 92.
[38] J.E. Anthony, D.L. Eaton, S.R. Parkin, Org. Lett. 4 (2002) 15.
[39] C.D. Simpson, J. Wu, M.D. Watson, K. Müllen, J. Mater. Chem. 14 (2004) 494.
[40] Z. An, J. Yu, S.C. Jones, S. Barlow, S. Yoo, B. Domercq, P. Prins, L.D.A. Siebbeles, B. Kippelen, S.R. Marder, Adv. Mater. 17 (2005) 2580.
[41] C. Videlet, J. Ackermann, P. Blanchard, J.M. Raimundo, P. Frére, M. Allian, R. Bettignies, E. Levilliain, J. Roncali, Adv. Mater. 15 (2003) 306.
[42] A.N. Sokolov, T.L. Friščić, R. MacGillivray, J. Am. Chem. Soc. 128 (2006) 2086.
[43] J.-M. Lehn, Supramolecular Chemistry, VCH, Weinheim, 1995, pp. 161–179.
[44] C.T. Seto, G.M. Whitesides, J. Am. Chem. Soc. 115 (1993) 905.
[45] G.M. Whitesides, J.P. Mathias, E.E. Simanek, J. Am. Chem. Soc. 116 (1994) 4326.
[46] T. Ishi-i, M. Crego-Calama, P. Timmerman, D.N. Reinhoudt, S. Shinkai, J. Am. Chem. Soc. 124 (2002) 14631.
[47] M. Weck, R. Fink, H. Ringsdorf, Langmuir 13 (1997) 3515.
[48] H. Koyano, P. Bissel, K. Yoshihara, K. Ariga, T. Kunitake, Chem. Eur. J. 3 (1997) 1077.
[49] X. Chen, Q.B. Xue, K.Z. Yang, Langmuir 11 (1995) 4082.
[50] G. Sui, J. Orbulescu, M. Mabrouki, M. Micic, R.M. Leblanc, S. Liu, R.A. Cormier, B.A. Gregg, J. Phys. Chem. B 106 (2002) 9335.
[51] T. Tang, J. Qu, K. Müllen, S.E. Webber, Langmuir 22 (2006) 26.
[52] Y. Kobuke, H. Miyaji, J. Am. Chem. Soc. 116 (1994) 4111.
[53] N. Nagata, S. Kugimiya, Y. Kobuke, Chem. Commun. (2000) 1389.
[54] Y. Chen, H.-G. Liu, P. Zhu, Y. Zhang, X. Wang, X. Li, J. Jiang, Langmuir 21 (2005) 11289.
[55] P. Smolenyak, R. Peterson, K. Nebesny, M. Tolrker, D.F. O'Brien, N.R. Armstrong, J. Am. Chem. Soc. 121 (1999) 8628.
[56] G. Sui, J. Orbulescu, M. Mabrouki, M. Micic, R.M. Leblanc, S. Liu, R.A. Cormier, B.A. Gregg, J. Phys. Chem. B 106 (2002) 9335.
[57] H.-G. Liu, D.-J. Qian, X.-S. Feng, Q.-B. Xue, K.-Z. Yang, Langmuir 16 (2000) 5079.
[58] K. Balakrishnan, A. Datar, T. Naddo, J. Huang, R. Oitker, M. Yen, J. Zhao, L. Zang, J. Am. Chem. Soc. 128 (2006) 7390.
[59] A.K. Maiti, R. Aroca, Y.J. Nagao, Raman Spectrosc. 24 (1993) 351.
[60] S. Rodriguez-Llorente, R. Aroca, J. Duff, Spectrochim. Acta 55A (1999) 969.
[61] K.I. Iverson, S.M. Casey, W. Seo, S.-W. Tam-Chang, B.A. Pindzola, Langmuir 18 (2002) 3510.
[62] S. Rodriguez-Llorente, R. Aroca, J. Duff, J.A. de Saja, Thin Solid Films 317 (1998) 129.
[63] A.J. Barnes, L. Legall, J. Lauransan, J. Mol. Struct. 56 (1979) 15.
[64] V. Parra, T.D. Cano, M.L. Rodríguez-Méndez, J.A. de Saja, R.F. Aroca, Chem. Mater. 16 (2004) 358.
[65] A.E. Clark, C. Qin, A.D.Q. Li, J. Am. Chem. Soc. 129 (2007) 7586.
[66] J. Feng, Y. Zhang, C. Zhao, R. Li, W. Xu, X. Li, J. Jiang, Chem. Eur. J. 14 (2008) 7000.
[67] A. Facchetti, M.-H. Yoon, C.L. Stern, H.E. Katz, T.J. Marks, Angew. Chem. Int. Ed. 42 (2003) 3900.
[68] P.A. Antunes, C.J.L. Constantino, R.F. Aroca, J. Duff, Langmuir 17 (2001) 2958.
[69] R. Aroca, C.J.L. Constantino, Langmuir 16 (2000) 5425.
[70] M. Yoneyama, M. Sugi, M. Saito, K. Ikegama, S. Kuroda, S. Iizima, Jpn. J. Appl. Phys. 25 (1986) 961.
[71] S.-G. Liu, G. Sui, R.A. Cormier, R.M. Leblanc, B.A. Gregg, J. Phys. Chem. B 106 (2002) 1307.
[72] E.H. Hadicke, F. Graser, Acta Crystallogr. C 42 (1986) 189.
[73] M.R. Wasielewski, J. Org. Chem. 71 (2006) 5051.
[74] K. Balakrishnan, A. Datar, R. Oitker, H. Chen, J. Zuo, L. Zang, J. Am. Chem. Soc. 127 (2005) 10496.
[75] T. van der Boom, R.T. Hayes, Y. Zhao, P.J. Bushard, E.A. Weiss, M.R. Wasielewski, J. Am. Chem. Soc. 124 (2002) 9582.
[76] M.J. Ahren, L.E. Sinks, B. Rybtchinski, W. Liu, B.A. Jones, J.M. Giaimo, A.V. Gusev, A. Goshe, D.M. Tiede, M.R. Wasielewski, J. Am. Chem. Soc. 126 (2004) 8284.