Poly-Ortho-Functionalizable Tetraarylporphycene Platform– Synthesis of Octacationic Derivatives Towards the Layer-by-Layer Design of Versatile Graphene Oxide Photoelectrodes

Wolfgang Brenner, Jenny Malig, Rubén D. Costa, Dirk M. Guldi,* and Norbert Jux*

Dedicated to the memory of Professor Christian Claessens

Porphycene, the first isolated and most stable constitutional isomer of porphyrin, was synthesized for the first time in 1986 by Vogel and co-workers.^[1] To this end, 2,7,12,17-tetra-*n*-propylporphycene is by far the most commonly studied porphycene derivative owing to its ease of synthesis and its remarkable solubility.^[2] In the early years, porphycenes were investigated as therapeutic agents in the field of photodynamic therapy.^[3] Given its structural similarity with porphyrins it is, however, surprising that porphycenes were hardly ever explored in areas such as catalysis,^[4] protein mimicry,^[5] and material science.^[6]

As far back as 1966, the concept of layer-by-layer (LbL) assemblies attracted considerable attention.^[7] The LbL concept gained new momentum in the 1990s. Here, multicomposite films were realized by the consecutive adsorption of polyanions and polycations^[8] offering a myriad of unique incentives by employing oppositely charged building blocks-molecules, particulates, and polymers. Charged polymers as LbL building blocks bring along a number of disadvantages. In particular, polymers are poly-disperse and usually do not adopt a defined and controlled shape and/or orientation within the deposited layers. Taken the aforementioned into concert, precise fine-tuning of the properties of polymeric thin films emerges as a real challenge. For example, Park et al. observed layers with varying charge density.^[9] Molecular rather than polymeric oligoelectrolytes assist in circumventing such drawbacks, as their structures and their properties are readily modified and adjusted. Such a strategy provided novel, hierarchically ordered materials with features applicable for electronic^[10] and mechanical uses.^[8,11]

In this context, we have recently reported the design, synthesis, and characterization of an 8-fold positively-charged porphyrin,^[12] followed later by an 8-fold negatively-charged porphyrin.^[13] By employing di-*ortho*-functionalized aryl rings as substituents in the meso-positions, aggregation was prevented and the charged substituents are well aligned. These poly-*ortho*substituted porphyrins have played an important role in solar

W. Brenner, J. Malig, Dr. R. D. Costa, Prof. D. M. Guldi, Dr. N. Jux Department of Chemistry & Pharmacy and Interdisciplinary Center for Molecular Materials Friedrich-Alexander-Universitat Erlangen-Nurnberg, 91054 Erlangen, Germany E-mail: dirk.guldi@chemie.uni-erlangen.de; norbert.jux@chemie.uni-erlangen.de



DOI: 10.1002/adma.201203459

energy conversion,^[13] electron donor-acceptor nanoensembles,^[14] and functionalization of nanoparticles.^[15] Recently, we have realized the implementation of these 8-fold negatively-charged porphyrins by means of LbL assembly to pyrene⁺ functionalized graphene.^[16] Importantly, the electron transfer dynamics were strongly impacted by the presence of electron accepting graphene. Encouraged by these results we adapted the aforementioned concept to porphycenes, which act as electron acceptors rather than as an electron donor.

www.MaterialsViews.co

In contrast to porphyrins, porphycenes display – besides the typical Soret band – absorption peaks with high extinction coefficients in the red region of the solar spectrum. This renders them very interesting candidates for the fabrication of solar cells. Surprisingly, up to now there has been only one publication dealing with the possible incorporation of porphycenes into solar cells.^[17]

Within the scope of the current study, we focused on an 8-fold positively-charged, water-soluble porphycene (Pc^{8+}) (Scheme 1). Pc^{8+} is, to the best of our knowledge, the most highly charged porphycene synthesized to date. To demonstrate the applicability of this electron acceptor in solar energy conversion devices, we tested negatively charged graphene oxide (GO), which has recently been used as a hole transport layer in polymer solar cells.^[18] Control over successfully assembling Pc^{8+} and GO to yield novel photoactive electrodes was possible through electrostatic interactions in solution and on electrode surfaces.

Since the pioneering work by Vogel et al.^[1] different routes for the synthesis of porphycenes have been explored, focusing on experimental facilitation,^[19] avoidance of unstable intermediates.^[20] exploration of an easily modifiable bipyrrole.^[21] and reduction of synthetic steps.^[22] The formation of appropriately substituted pyrroles is more challenging and requires the corresponding aldehydes as building blocks and starts with the formation of the respective nitroolefins followed by a Barton-Zard reaction, delivering the desired pyrroles in yields of up to 90%.^[23] Due to steric demands imposed by aldehyde 1 (Scheme 1), the corresponding nitro-olefin could not be prepared at all. In a similar approach, the ethyl cinnamate derived from 1 for the Sanchez-García's route was assumed not to be accessible either.^[22] Finally, the desired pyrrole was synthesized under more drastic conditions. In a slight modification of the pyrrole formation described by Matsumoto et al.,^[24] DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) was added to a mixture of aldehyde 1 (Scheme 1) and ethyl isocyanoacetate.^[12] The latter led to a 20% yield for a 24 hours reaction. In the context of iodination of the free α -position of the pyrrole, we modified a procedure first

ADVANCED MATERIAL



www.MaterialsViews.com

MATERIALS www.advmat.de



Scheme 1. Synthesis of porphycene Pc^{8+} . In the boxes photophysically investigated porphycenes are shown.

described by Dolphin et al.^[25] In particular, by dissolving pyrrole in acetic acid and treating it with an excess of iodine monochloride afforded α -iodinated pyrrole **3** in quantitative yields.^[26] Following iodination, Ullmann coupling was conducted before bipyrrole **4** was saponified and decarboxylated. The unsubstituted bipyrrole **5** was then subjected to Vilsmeier-Haack formylation.

Mass spectra analysis confirmed that during the formylation reaction with DMF/POCl₃ substitution of some methoxy groups by chloride atoms took place. Owing to the stability of halogenated compounds under McMurry conditions,^[27] a lowvalent titanium-mediated coupling procedure was employed. For analysis, **PcOMe** was separated by column chromatography. The steric demand of the substituents is derived from the ¹H NMR spectra, especially from the signals of the phenyl-CH₂ groups (Figure S1). Interestingly, the C–C rotation centered at the phenyl/pyrrole connection is not hindered in pyrrole **2** (one singlet), but inhibited in iodopyrrole **3** and bipyrrole tetracarboxylic ester **4** (two doublets). In stark contrast, removing the esters in the 3,3',5,5'-positions releases the rotation (one singlet), before the signals appear again as two doublets in the resulting porphycene **PcOMe**.

Following the McMurry reaction, the mixture of different porphycenes **PcOMe/7** was treated with hydrobromic acid in acetic acid for seven days to yield exclusively porphycene 8

bearing eight bromomethyl substituents. The need for such a long reaction time relates to the slow replacement of chloromethyl with bromomethyl groups. With the poly-*ortho*-brominated porphycene 8 in hands, the 8-fold positively-charged tetraarylporphycene Pc^{8+} was obtained by heating with *tert*-butylpyridine in toluene at reflux temperature.

The electronic properties of porphycene **PcOMe** and the positively charged porphycene **Pc**⁸⁺ in the ground state resemble those known for tetrakis-(*tert*-butylphenyl) porphycene (**Pc**).^[26] As shown in **Figure 1**, the Soret- and Q-bands are 4 nm (284 cm⁻¹) and 14 nm (328 cm⁻¹) hypsochromically shifted in **PcOMe** with respect to **Pc**. In agreement with solvatochromic effects, the absorption bands of **Pc**⁸⁺ are 5 nm (354 cm⁻¹) and 7 nm (166 cm⁻¹) red-shifted with respect to **PcOMe**.

Next, the electrochemical features were determined for Pc^{8+} (10⁻⁴ M) in acetonitrile and for PcOMe (10⁻⁴ M) in THF with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte and Fc/Fc⁺ as standard versus Ag/Ag⁺. In terms of reduction, two quasi-reversible reduction steps evolve at -0.65 and -0.93 V for **PcOMe** as well as at -0.41 and -1.14 V for **Pc⁸⁺**. In terms of oxidation, the two oxidation steps at +0.86 and +1.24 V for **PcOMe** as well as at +0.86 and +1.27 V for **Pc⁸⁺** are quasi-reversible.

Initial insights into the excited state characteristics of PcOMe and Pc^{8+} stem from fluorescence spectroscopy. When compared





Figure 1. Upper part–absorption spectra of **PcOMe** (light grew) in THF, **Pc**⁸⁺ (black) in THF, and **Pc** (dark grey) in THF. Central part–3D fluorescence of **Pc**⁸⁺ in water. Lower part–time-correlated single-photon counting of **Pc**⁸⁺ in water in the absence (black) and in the presence of variable concentrations of GO (dark grey to light grey)–excitation wavelength of 403 nm and emission wavelength of 650 nm.

to **Pc**, the fluorescence maxima are hypsochromically shifted to 652 nm for **PcOMe** (in THF) and 660 nm for **Pc⁸⁺** (in water), which agrees with the ground state features (vide supra). The fluorescence quantum yields were determined by using the gradient method^[28] as 0.9 and 0.4 for **PcOMe** and **Pc⁸⁺**, respectively. Finally, the major components in the fluorescent excited state decay are 6.5 ns (**PcOMe**) and 6.2 ns (**Pc⁸⁺**).



Our initial investigations focused on titration assays of porphycene Pc^{8+} and graphene oxide (GO) monitoring the changes of the absorption and emission features of Pc^{8+} as different concentrations of GO were added. In the ground state, an increase of the absorbance was measured when GO was present (Figure S2) suggesting the formation of Pc^{8+} /GO electron donor-acceptor hybrids. In the excited state, the fluorescence of Pc^{8+} is gradually quenched upon GO addition (Figure S2). The latter reflects in readily formed Pc^{8+} /GO either an effective transduction of excited state energy from photoexcited Pc^{8+} to GO or an effective electron transfer from GO to photoexcited Pc^{8+} .^[29]

As a complement to the latter, the changes in fluorescence lifetimes were monitored for different Pc^{8+}/GO ratios (Figure 1). In the absence of GO, the fluorescence time profile of Pc^{8+} , as determined, for example, at the 650 nm fluorescence maximum by exciting at 403 nm, is dominated by long-lived component of 6.2 ns (94%) (vide infra). Upon adding GO, only a short-lived component, which is, however, masked by the instrumental resolution of 0.1 ns, is seen in the fluorescence decay of Pc^{8+} . We consider the latter as yet another attest for the association of Pc^{8+} and GO owing to electrostatic interactions.

To exclude aggregation due to charge neutralization a solution of Pc^{8+}/GO was drop casted onto a silicon wafer and tested by means of atomic force microscopy (Figure S3). Given the fact that single layer flakes of GO are observed indicates that Pc^{8+}/GO is non-aggregated.

Encouraged by these results, we turned to fabricate photoelectrochemical cells with photoactive indium tin oxide (ITO) electrodes modified by the sequential LbL deposition of Pc8+ and GO, that is, ITO/PDDA/PSS/(Pc⁸⁺/GO)_x. As reference electrodes, GO was replaced with PSS to result in ITO/PDDA/PSS/ $(\mathbf{Pc}^{8+}/\mathrm{PSS})_{x}$. Here, PDDA is poly-(diallyl-dimethylammonium), PSS is poly-(sodium-4-styrenesulfonate), and x varies from 1 to 14. To complete the devices we utilized polysulfide electrolytes (i.e., equimolar 3 M Na₂S/S/NaOH) and Cu₂S-based counter electrodes-see Supporting Information. The LbL formation was monitored after each deposition step by absorption and fluorescence spectroscopy. Of particular importance is the fact that the resulting absorption spectra of Pc8+ in both ITO/PDDA/PSS/ $(Pc^{8+}/GO)_x$, and ITO/PDDA/PSS/ $(Pc^{8+}/PSS)_x$ resemble those seen in aqueous solutions and that the overall absorptions increase linearly as a function of deposition steps (Figures 2, S4, and S5). In complementary experiments the film thickness was probed by ellipsometric measurements (Figure 2). To this end, we note a linear relationship, which corroborates the absorption measurements. In ITO/PDDA/PSS/(Pc⁸⁺/GO)_x a quantitative fluorescence quenching of Pc^{8+} is discernable upon 403 nm excitation. This is in good agreement with the homogeneous experiments performed in water (vide supra). Finally, to confirm the notion of a controlled two-dimensional film growth, scanning electron microscopy (SEM) images were performed. The latter shows a good coverage of the ITOs featuring the absence of GO aggregation (Figures 2 and S6). As such, we conclude the successful control over the homogeneous LbL deposition as means to integrate Pc8+ and GO onto photoelectrodes.

The modified ITO/PDDA/PSS/ $(Pc^{8+}/GO)_x$ reveal promising photoresponse profiles under AM 1.5 conditions, which increase as a function of Pc^{8+}/GO sandwich layers (Figure 3). Starting at around 10 layers, we note a plateau in the performance

www.advmat.de





Figure 2. Upper part-plot of absorbances at 385 and 650 nm of Pc^{8+} / GO LbL assemblies on ITO/PDDA/PSS with increasing number of Pc^{8+} / GO sandwich layers-up to 14. The inset shows the absorption spectra. Central part-ellipsometric thickness of Pc^{8+} /GO LbL assemblies on Si/ PDDA/PSS as a function of Pc^{8+} /GO sandwich layers-up to 14. Lower part-SEM image of Pc^{8+} /GO LbL assembly on ITO/PDDA/PSS.

reaching short-circuit current densities (J_{sc}) between 100 and 120 μ A/cm² and open-circuit voltages (V_{oc}) of around 0.15 V. Under monochromatic illumination, that is, the incident photon to charge carrier efficiency (IPCE) spectrum, a good resemblance with the absorption features prompts to the photosensitizing features of **Pc**⁸⁺ (Figure 3). Next, the direction of charge flow was probed by systematically varying the electrolyte composition from an electron mediator (i.e., Na₃PO₄ solution purged with O₂ and Ar) to a hole mediator (i.e., mixture of



Figure 3. Upper part–photoaction spectrum of a ITO/PDDA/PSS/(**Pc**⁸⁺/GO)₁₄ photoelectrode under AM 1.5 conditions. Central part – photocurrent-voltage characteristics of ITO/PDDA/PSS/(**Pc**⁸⁺/GO)_x photoelectrodes with increasing number of **Pc**⁸⁺/GO sandwich layers–up to 14–under AM 1.5 conditions. Lower part – photocurrent-voltage characteristics of ITO/PDDA/PSS/(**Pc**⁸⁺/PSS)_x photoelectrodes with increasing number of **Pc**⁸⁺/PSS sandwich layers–up to 10–under AM 1.5 conditions.

 Na_3PO_4 and sodium ascorbate purged with O_2 and Ar) rather than polysulfide (Figure S7).

In the absence of GO, namely in ITO/PDDA/PSS/(Pc^{8+} /PSS)_x devices, free charge carriers are generated through interfacial interactions between photoexcited Pc^{8+} and the redox electrolyte. Such a mechanism is, however, only effective when a maximum of two Pc^{8+} /PSS sandwich layers are present. Charge formation at the interface, charge transport through the sandwich layers, and charge collection at the ITO electrodes is blocked upon increasing the number of layers. As a matter of

MATERIA

www.advmat.de

fact, the latter is further corroborated by the lack of appreciable photocurrents upon increasing the number of \mathbf{Pc}^{8+} /PSS sandwich layers (Figure 3). Therefore, the benefits that stem from collecting and transporting electrons through the different GO layers is demonstrated, on one hand, by a direct comparison with the ITO/PDDA/PSS/(\mathbf{Pc}^{8+} /PSS)_x devices and, on the other hand, by the increase of the overall performances for the ITO/PDDA/PSS/(\mathbf{Pc}^{8+} /GO)_x devices upon increasing the number of \mathbf{Pc}^{8+} /GO sandwich layers (Figure 3).

In summary, a sterically demanding tetraarylporphycene PcOMe has been synthesized and characterized. The synthetic route was modified at two critical steps, namely the formation of the pyrrole and the subsequent iodination. The Vilsmeier-Haack formylation led to a mixture of porphycenes (PcOMe and 7), which was converted into the all-brominated porphycene 8 (Scheme 1). 8 offers a wide variety of possibilities regarding further functionalization. Within the scope of the current study we concentrated on the 8-fold positively-charged, water-soluble porphycene Pc^{8+} . Importantly, Pc^{8+} displays the characteristic traits of porphycenes such as high extinction coefficients, high fluorescence quantum yields, and ease of reduction. In fact, these features are true assets in the context of interacting with GO to yield electron acceptor-donor ensembles Pc^{8+} /GO. In the final experiments, Pc^{8+} and GO were employed to construct LbL assemblies on ITO electrodes. The performance of the corresponding photoelectrochemical devices highlights, for the first time, the suitability of functionalized porphycenes as new building blocks towards future nanohybrid materials for solar cell applications.

Experimental Section

More information on synthetic, spectroscopical, and electrochemical characterization details as well as AFM images are included in the Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

For financial support the DFG (SFB 953), ICMM, and GSMS are gratefully acknowledged. R.D.C. acknowledges the Humboldt Foundation for support.

Received: August 20, 2012 Revised: October 23, 2012 Published online: December 13, 2012

- E. Vogel, M. Köcher, H. Schmickler, J. Lex, Angew. Chem. Int. Ed. 1986, 25, 257–259.
- [2] E. Vogel, M. Balci, K. Pramod, P. Koch, J. Lex, O. Ermer, Angew. Chem. Int. Ed. 1987, 26, 928–931.
- [3] a) C. Richert, J. M. Wessels, M. Mueller, M. Kisters, T. Benninghaus, A. E. Goetz, J. Med. Chem. 1994, 37, 2797–2807; b) V. Gottfried,



www.MaterialsViews.com

R. Davidi, C. Averbuj, S. Kimel, J. Photochem. Photobiol. B: Biology 1995, 30, 115–121.

- [4] a) T. Hayashi, K. Okazaki, N. Urakawa, H. Shimakoshi, J. L. Sessler,
 E. Vogel, Y. Hisaeda, *Organometallics* 2001, 20, 3074–3078;
 b) W.-C. Lo, C.-M. Che, K.-F. Cheng, T. C. W. Mak, *Chem. Commun.* 1997, 1205–1206.
- [5] a) T. Hayashi, H. Dejima, T. Matsuo, H. Sato, D. Murata, Y. Hisaeda, *J. Am. Chem. Soc.* 2002, *124*, 11226–11227; b) T. Hayashi, D. Murata, M. Makino, H. Sugimoto, T. Matsuo, H. Sato, Y. Shiro, Y. Hisaeda, *Inorg. Chem.* 2006, *45*, 10530–10536; c) T. Matsuo, H. Dejima, S. Hirota, D. Murata, H. Sato, T. Ikegami, H. Hori, Y. Hisaeda, T. Hayashi, *J. Am. Chem. Soc.* 2004, *126*, 16007–16017; d) H. Nakashima, J.-y. Hasegawa, H. Nakatsuji, *J. Comput. Chem.* 2006, *27*, 1363–1372; e) T. Matsuo, T. Tsuruta, K. Maehara, H. Sato, Y. Hisaeda, T. Hayashi, *Inorg. Chem.* 2005, *44*, 9391–9396.
- [6] J.-M. Barbe, P. Richard, M. A. Aukauloo, C. Lecomte, P. Petit, R. Guilard, Chem. Commun. 1994, 2757–2758.
- [7] R. K. Iler, J. Colloid Interface Sci. 1966, 21, 569-594.
- [8] G. Decher, Science 1997, 277, 1232-1237.
- [9] S. Y. Park, M. F. Rubner, A. M. Mayes, Langmuir 2002, 18, 9600–9604.
- [10] a) P. K. D. D. P. Pitigala, M. K. I. Seneviratne, V. P. S. Perera, K. Tennakone, *Langmuir* 2004, 20, 5100–5103; b) S. Ponader, K. Rosenlehner, E. Vairaktaris, C. von Wilmowsky, K. Schlegel, F. Neukam, C. Schmidt, T. Schunk, A. Hirsch, E. Nkenke, *J. Mater. Sci.: Mater. Med.* 2009, 20, 2455–2463.
- [11] D. M. Kaschak, J. T. Lean, C. C. Waraksa, G. B. Saupe, H. Usami, T. E. Mallouk, J. Am. Chem. Soc. 1999, 121, 3435–3445.
- [12] N. Jux, Org. Lett. 2000, 2, 2129–2132.
- [13] D. M. Guldi, I. Zilbermann, G. Anderson, A. Li, D. Balbinot, N. Jux, M. Hatzimarinaki, A. Hirsch, M. Prato, *Chem. Commun.* 2004, 726–727.
- [14] D. M. Guldi, G. N. A. Rahman, J. Ramey, M. Marcaccio, D. Paolucci, F. Paolucci, S. Qin, W. T. Ford, D. Balbinot, N. Jux, N. Tagmatarchis, M. Prato, *Chem. Commun.* **2004**, 2034–2035.
- [15] J.-F. Gnichwitz, R. Marczak, F. Werner, N. Lang, N. Jux, D. M. Guldi, W. Peukert, A. Hirsch, J. Am. Chem. Soc. 2010, 132, 17910–17920.
- [16] J. Malig, C. Romero-Nieto, N. Jux, D. M. Guldi, Adv. Mater. 2012, 24, 800–805.
- [17] Y. Yamada, T. Okujima, N. Ono, D. Kuzuhara, JP2010077054.
- [18] S.-S. Li, K.-H. Tu, C.-C. Lin, C.-W. Chen, M. Chhowalla, ACS Nano 2010, 4, 3169–3174.
- [19] S. Nonell, N. Bou, J. Borrell, J. Teixidó, A. Villanueva, A. Juarranz, M. Cañete, *Tetrahedron Lett.* **1995**, *36*, 3405–3408.
- [20] A. Gavalda, J. I. Borrell, J. Teixido, S. Nonell, O. Arad, R. Grau, M. Canete, A. Juarranz, A. Villanueva, J. C. Stockert, J. Porphyrins Phthalocyanines 2001, 5, 846–852.
- [21] O. Arad, J. Morros, X. Batllori, J. Teixido, S. Nonell, J. I. Borrell, Org. Lett. 2006, 8, 847–850.
- [22] D. Sánchez-García, J. I. Borrell, S. Nonell, Org. Lett. 2009, 11, 77–79.
- [23] M. Stepien, B. Donnio, Jonathan L. Sessler, Angew. Chem. Int. Ed. 2007, 46, 1431–1435.
- [24] M. Suzuki, M. Miyoshi, K. Matsumoto, J. Org. Chem. 1974, 39, 1980.
- [25] J. B. Paine, D. Dolphin, J. Org. Chem. 1988, 53, 2787-2795.
- [26] W. Brenner, J. Malig, D. Oelsner, D. M. Guldi, N. Jux, J. Porphyrins Phthalocyanines 2012, 16, 651–662.
- [27] J. E. McMurry, Chem. Rev. 1989, 89, 1513-1524.
- [28] J. Y. Horiba, http://www.horiba.com/us/en/scientific/products/fluorescence-spectroscopy/application-notes/quantum-yields/, 2002.
- [29] In reference experiments with poly-(sodium-4-styrenesulfonate) (PSS) and Pc⁸⁺ no fluorescence quenching was noted.