Liquid Crystals

International Edition: DOI: 10.1002/anie.201705137 German Edition: DOI: 10.1002/ange.201705137

Diketopyrrolopyrrole Columnar Liquid-Crystalline Assembly Directed by Quadruple Hydrogen Bonds

Bartolome Soberats,* Markus Hecht, and Frank Würthner*

Abstract: A diketopyrrolopyrrole (DPP) dye self-assembles via a unique hydrogen-bonding motif into an unprecedented columnar liquid-crystalline (LC) structure. X-ray and polarized FTIR experiments reveal that the DPPs organize into a one-dimensional assembly with the chromophores oriented parallel to the columnar axis. This columnar structure is composed of two π - π -stacked DPP dimers with mirror-image configurations that stack alternately through quadruple hydrogen bonding by 90° rotation. This exotic packing is dictated by the complementarity between H-bonds and the steric demands of the wedge-shaped groups attached at the core. This novel LC supramolecular material opens a new avenue of research on DPP dye assemblies with photofunctional properties tailored by H-bonding networks.

Self-assembly of organic dyes has emerged as a promising approach for the rational design of functional materials.^[1-8] This is commonly performed by encoding information in the molecular building blocks to control their assembly process and packing arrangement which, in turn, define the properties. In this regard, among non-covalent interactions particularly hydrogen bonds (H-bonds) evolved as most useful for the creation of functional non-covalent architectures, such as supramolecular polymers,^[9-12] gels,^[13] and liquid crystals.^[14-20] The control of self-assembly directed by H-bonds has been widely investigated for many dyes such as, for instance, porphyrins,^[21] BODIPYs,^[22] pyrenes,^[23] merocyanines,^[24] naphthalene, and pervlene bisimides (PBIs),^[25] giving access to assemblies with desired functional properties and characteristic optical signatures such as H- and J-type exciton couplings.^[26-28]

Interestingly, despite the wide application of diketopyrrolopyrrole (DPP) dyes as the most-brilliant red color pigments^[29,30] (for example, Pigment Red (PR) 254, nicknamed "Ferrari Red") and semiconductors in organic electronics and photovoltaics,^[31,32] the self-assembly of DPPs in solution and in the liquid-crystalline (LC) state has been barely explored.^[33] This is particularly surprising as the crystal

 [*] Dr. B. Soberats, Prof. Dr. F. Würthner Center for Nanosystems Chemistry (CNC) & Bavarian Polymer Institute (BPI), Universität Würzburg Theodor-Boveri-Weg, 97074 Würzburg (Germany) E-mail: bartolome.soberats_reus@uni-wuerzburg.de wuerthner@uni-wuerzburg.de
 M. Hecht, Prof. Dr. F. Würthner Institut für Organische Chemie, Universität Würzburg Am Hubland, 97074 Würzburg (Germany)
 Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/anie.201705137.

Angew. Chem. Int. Ed. 2017, 56, 1-5

© 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

structure of PR 254 reveals an attractive supramolecular motif based on double hydrogen-bonding between the selfcomplementary lactam units combined with π - π -stacking interactions between the DPP π -scaffolds.^[34] However, the perfect interplay of these non-covalent forces establishes the pigment character, that is, complete insolubility in any solvent. Upon alkylation of the lactam nitrogen, well-soluble dyes are generated, which in contrast to their PBI^[25b] counterparts show little propensity for aggregation owing to weak π - π interactions between the rather small DPP π scaffolds. Herein we report the first example for the selfassembly of DPP dyes guided by H-bonding between nonalkylated lactam units, leading to a columnar LC phase with an unprecedented 1D packing formed by quadruple Hbonded DPP dimers (Figure 1). Surprisingly, we found that this assembly is formed through the alternate stacking of two DPP dimers with mirror image configuration (dimer A and



Figure 1. a) The chemical structure of **DPP 1**. b) Illustration of the molecular self-assembly of **DPP 1** into a columnar hexagonal LC phase, where the DPP molecules organize in stacked dimers forming H-bonds along the columnar axis. This assembly mode requires the stacking of two DPP dimers (dimer A and dimer B), which are mutual enantiomers. The alternate stacking by 90° rotation of dimer A and dimer B induces quadruple H-bonding interactions. The stacking by 90° rotation of one type of dimers would lead to H-bonding mismatch.

dimer B; Figure 1b) that show a complementary H-bonding topology when they stack by 90° rotation (Figure 1b).

The molecular design of **DPP 1** (Figure 1a) bearing two 3,4,5-tridodecyloxyphenyl wedge-shaped moieties at the 3and 6-position of the core and two free N-H groups at the lactam positions was guided by our previously established design principles for the H-bond-directed self-assembly of PBI dyes.^[35] The wedge-shaped part is expected to provide solubility and mesogenic features to the compound, while the free N-H and the carbonyl groups are supposed to direct the self-assembly by H-bonding interactions (Figure 1). DPP 1 was obtained in a straightforward way as a red waxy solid by slight modifications of a previously described procedure (Supporting Information).^[36] The UV/Vis spectrum of **DPP** 1 in chloroform showed a characteristic absorption band at 519 nm with vibronic progressions and a weaker band at 352 nm,^[29-34] while the spectrum is broadened in the solid state (Supporting Information, Figure S2).

The LC properties of **DPP 1** were examined by polarizing optical microscopy (POM), differential scanning calorimetry (DSC), and middle- and wide-angle X-ray scattering (MAXS and WAXS) experiments. POM observation and DSC experiments revealed the formation of two LC phases, a lowtemperature phase from 0 to 45°C and a high-temperature phase from 45 up to 336 °C, at which the material decomposes (Supporting Information, Figures S3 and S4). The X-ray diffraction pattern of DPP 1 at 30°C shows three broad reflections. owing to the broadness of the signals, this phase was not clearly identified, but the two intense reflections in the small-angle region are consistent with the 200 and 110 signals of a columnar rectangular (Col_r) phase (Supporting Information, Figure S6). In contrast, the X-ray pattern at 80°C clearly shows the 100, 110, 200, 210, and 310 characteristic reflections of a columnar hexagonal (Col_h) lattice (a =28.5 Å) (Figure 2a). In both cases, the presence of a diffused halo indicates liquid-like disordered aliphatic chains.

The relative orientation of the DPP cores in both columnar assemblies was studied by polarized FTIR experiments and POM on aligned samples of DPP 1 at 30 and 80 °C (Figure 3: Supporting Information, Figures S5 and S7). The sample for IR studies was aligned by friction transfer of an extruded fiber of **DPP 1** on a KBr plate, which produced the orientation of the columns parallel to the substrate and the shearing direction. This was confirmed in the POM experiments of the aligned samples on glass plates (Supporting Information, Figure S5).^[14,15,17] Importantly, the FTIR spectra of **DPP 1** show the NH stretching vibration at 3170 cm^{-1} , which indicates that the NH groups are H-bonded,^[35,37] as it is expected for a DPP with unsubstituted lactams.^[34] The polarized FTIR spectra of the sheared sample show that the NH peak is more intense when the columnar phase is homogeneously aligned in the parallel direction of the polarizer, and practically disappears when the polarizer is oriented perpendicularly to the aligned sample (Figure 3a; Supporting Information, Figure S7). These experiments revealed that the lactam functionalities and subsequently the π -surfaces are oriented parallel to the columnar axis (Figure 3b).



Figure 2. a) Integrated intensities along the equator of the WAXS pattern of **DPP 1** at 80 °C. b),c) WAXS patterns of an extruded fiber of **DPP 1** at 80 °C with the fiber axis lying (b) and standing (c). Direction of the fiber is indicated with yellow arrows. Layer lines (*hkl*) are indicated along the meridian.



Figure 3. a) Polarized FTIR spectra of an aligned sample of **DPP 1** at 80 °C with the polarizer parallel (red line) and perpendicular (black line) to the direction of the alignment. b) Representation of the homogenously aligned **DPP 1** columnar assembly and the relative orientation of the DPP molecules.

To gain deeper insights into the self-assembled structure, we analyzed in detail the WAXS patterns of lying and standing fibers of **DPP 1** at 80 °C (Figure 2b,c). The diffuse signal at 4 Å on the equator (Figure 2b) suggests low correlated core–core interactions orthogonal to the columnar axis.^[35b] This is in accordance with the orientation of the DPP cores parallel to the columnar axis as it is also confirmed by FTIR experiments (Figure 3). Moreover, the observation of reflections in the quadrants and the meridian of the X-ray pattern allowed us to get more details about the organization of the molecules into the columnar assembly. A strong signal on the meridian at 7 Å matches well with the length of a DPP from NH to NH (6.0 Å; Supporting Information, Figure S8).

www.angewandte.org

2

© 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

K These are not the final page numbers!

This reflection was assigned to the layer line hk^2 (Figure 2c), while the off-meridional reflections appearing at a distance corresponding to 14 Å (twice the length of the DPP) were assigned to layer line hk1 (Figure 2c). The layer line hk4could also be observed on the meridian in the wide-angle region. These observations indicate a correlation of every second molecule along the columns, which implies a rotation of 90° between DPPs of adjacent strata.^[38] The number of molecules per columnar slice (h = 7 Å) was estimated to be two, considering the cell parameters (a = 28.5 Å) and assuming a reasonable density of 1 g cm⁻³ (Supporting Information).^[35b] Accordingly, the columnar assembly is composed of $\pi\text{-stacked}$ DPP dimers that are in turn stacked along the column by 90° rotation (Figure 1b). A similar arrangement of DPP dyes was observed in low temperature (30 °C) Col_r phase as revealed by WAXS and polarized FTIR experiments (Supporting Information, Figures S6 and S7). We assume that this rotation of the dimeric DPP axial subunits is imposed by the steric demand of the wedge-shape groups and space filling effects.[38,39]

According to the parameters obtained from X-ray experiments, we modeled a packing structure for **DPP 1** in the Col_h phase using the software package Materials Studio. We assume that the DPP cores are in the center of the columns, connected by H-bonds and surrounded by the alkyl chains (Figure 1). For the modeling studies, we focused on the DPP part and therefore the peripheral dodecyl chains were omitted to simplify the system. The model assembly was constructed starting from a co-facial DPP dimer where the carbonyl and NH groups are alternated to minimize repulsions (Supporting Information, Figure S9). The next two DPPs were rotated by 90°, according to the X-ray data, and connected by H-bonds to the initial dimer. The structure was completed with the stacking of eight molecules, paired in four stacked DPP dimers with the cores parallel to the columnar axis. The geometry was optimized by the force-field COMPASS using the Ewald summation method. The optimized structure shows a negative non-bonding interaction energy, which suggests a stable assembly. Figure 4a depicts the resulting minimized structure that shows a columnar stack of four DPP dimers connected via quadruple H-bonds. More interestingly, our modeling studies reveal that this supramolecular assembly via complementary H-bonds entails the 1D stack of two stereochemically distinct DPP dimers,^[40] dimer A and dimer B (Figure 4b). Each dimer presents a different topology of the H-bonding units (carbonyl and NH groups). Thus, the perfect H-bond matching to form the columnar structure from dimers rotated by 90° (according to X-ray data) is only achieved by the alternation of dimer A and dimer B (Figure 4c). In contrast, the formation of an H-bonded network is not possible by the stack of one type of dimers (Figure 4c). The steric demands of DPP 1, which imposes the 90° rotation of dimers, and the complementarity of the H-bonding between dimeric units determine this unprecedented columnar arrangement. Retrostructural analysis of the minimized structure was performed utilizing the program CLEARER (Supporting Information, Figure S10).^[41] Pleasingly, the simulated X-ray pattern shows a very good match with the



Figure 4. a) Geometry-optimized structure of the DPP 1 assembly showing the alternate stacking of dimers. b) Structure of dimer A and dimer B found in the assembled structure of DPP 1. c) Illustration of the H-bonding mismatch (left) and match (right) in B–B and A–B stacked dimers, respectively. The H-bonds are illustrated as double arrows, while the H-bond mismatches with red crossed double arrows. The tridodecyloxyphenyl groups of the DPPs were omitted for clarity. DPP cores red, O blue, N–H green. d) Superposition of the simulated diffraction pattern obtained by CLEARER and the MAXS pattern of DPP 1 at 80°C.

reflections of the experimental MAXS pattern, supporting the proposed structure (Figure 4d).

In summary, we discovered an unprecedented supramolecular motif that guides the formation of a liquidcrystalline 1D assembly of **DPP 1** by quadruple hydrogen bonding between π -stacked DPP dimers. This complex assembly is formed by the stack of two complementary dimers where the diketopyrrolopyrrole π -cores lie parallel to the columnar axis. This uncommon organization in columnar liquid crystals warrants further exploration, which includes research on the growth of functional supramolecular fibers in solution and the application of such novel diketopyrrolopyrrole self-assemblies in functional materials.

www.angewandte.org

Acknowledgements

We thank Prof. Matthias Lehmann (Würzburg) for helpful discussions and the Bavarian State Ministry of Education, Science and the Arts for generous support for the newly established Key Laboratory for Supramolecular Polymers at the Center for Nanosystems Chemistry.

Conflict of interest

The authors declare no conflict of interest.

Keywords: diketopyrrolopyrroles · dyes/pigments · hydrogen bonds · liquid crystals · self-assembly

- Z. Chen, A. Lohr, C. R. Saha-Möller, F. Würthner, *Chem. Soc. Rev.* 2009, 38, 564–584.
- [2] B. M. Rosen, C. J. Wilson, D. A. Wilson, M. Peterca, M. R. Imam, V. Percec, *Chem. Rev.* 2009, 109, 6275–6540.
- [3] T. Aida, E. W. Meijer, S. I. Stupp, Science 2012, 335, 813-817.
- [4] A. Ajayaghosh, V. K. Praveen, Acc. Chem. Res. 2007, 40, 644– 656.
- [5] A. Kaeser, A. P. H. J. Schenning, Adv. Mater. 2010, 22, 2985– 2997.
- [6] S. Yagai, Bull. Chem. Soc. Jpn. 2015, 88, 28-58.
- [7] Y. Sagara, S. Yamane, M. Mitani, C. Weder, T. Kato, *Adv. Mater.* 2016, 28, 1073–1095.
- [8] E. Krieg, M. M. C. Bastings, P. Besenius, B. Rybtchinski, *Chem. Rev.* 2016, 116, 2414–2477.
- [9] T. F. A. De Greef, M. M. J. Smulders, M. Wolffs, A. P. H. J. Schenning, R. P. Sijbesma, E. W. Meijer, *Chem. Rev.* 2009, 109, 5687-5754.
- [10] P. Besenius, J. Polym. Sci. Part A J. Polym. Sci. A Polym. Chem. 2017, 55, 34–78.
- [11] L. Yang, X. Tan, Z. Wang, X. Zhang, Chem. Rev. 2015, 115, 7196–7239.
- [12] C. Rest, R. Kandanelli, G. Fernández, Chem. Soc. Rev. 2015, 44, 2543–2572.
- [13] S. S. Babu, V. K. Praveen, A. Ajayaghosh, *Chem. Rev.* 2014, 114, 1973–2129.
- [14] Handbook of Liquid Crystals, 2nd ed. (Eds.: J. W. Goodby, P. J. Collings, T. Kato, C. Tschierske, H. Gleeson, P. Raynes), Wiley-VCH, Weinheim, 2014.
- [15] T. Kato, N. Mizoshita, K. Kishimoto, Angew. Chem. Int. Ed. 2006, 45, 38–68; Angew. Chem. 2006, 118, 44–74.
- [16] C. Tschierske, Angew. Chem. Int. Ed. 2013, 52, 8828–8878; Angew. Chem. 2013, 125, 8992–9047.
- [17] T. Kato, M. Yoshio, T. Ichikawa, B. Soberats, H. Ohno, M. Funahashi, Nat. Rev. Mater. 2017, 2, 17001.
- [18] D. J. Broer, C. M. W. Bastiaansen, M. G. Debije, A. P. H. J. Schenning, Angew. Chem. Int. Ed. 2012, 51, 7102–7109; Angew. Chem. 2012, 124, 7210–7218.
- [19] T. Wöhrle, I. Wurzbach, J. Kirres, A. Kostidou, N. Kapernaum, J. Litterscheidt, J. C. Haenle, P. Staffeld, A. Baro, F. Giesselmann, S. Laschat, *Chem. Rev.* 2016, *116*, 1139–1241.
- [20] S. Sergeyev, W. Pisula, Y. H. Geerts, Chem. Soc. Rev. 2007, 36, 1902–1929.

- [21] J. A. A. W. Elemans, R. van Hameren, R. J. M. Nolte, A. E. Rowan, Adv. Mater. 2006, 18, 1251–1266.
- [22] A. Rödle, B. Ritschel, C. Mück-Lichtenfeld, V. Stepanenko, G. Fernández, *Chem. Eur. J.* **2016**, *22*, 15772–15777.
- [23] Y. Sagara, T. Kato, Nat. Chem. 2009, 1, 605-610.
- [24] a) S. Yagai, Y. Nakano, S. Seki, A. Asano, T. Okubo, T. Isoshima, T. Karatsu, A. Kitamura, Y. Kikkawa, *Angew. Chem. Int. Ed.* **2010**, 49, 9990–9994; *Angew. Chem.* **2010**, 122, 10186–10190;
 b) S. Yagai, S. Okamura, Y. Nakano, M. Yamauchi, K. Kishikawa, T. Karatsu, A. Kitamura, A. Ueno, D. Kuzuhara, H. Yamada, T. Seki, H. Ito, *Nat. Commun.* **2014**, 5, 4013.
- [25] a) A. Das, S. Ghosh, *Chem. Commun.* 2016, *52*, 6860–6872; b) F.
 Würthner, C. R. Saha-Moller, B. Fimmel, S. Ogi, P. Leowanawat, D. Schmidt, *Chem. Rev.* 2016, *116*, 962–1052.
- [26] E. G. McRae, M. J. Kasha, Chem. Phys. 1958, 28, 721-722.
- [27] F. C. Spano, Acc. Chem. Res. 2010, 43, 429-439.
- [28] F. Würthner, T. E. Kaiser, C. R. Saha-Möller, Angew. Chem. Int. Ed. 2011, 50, 3376–3410; Angew. Chem. 2011, 123, 3436–3473.
- [29] M. Grzybowski, D. T. Gryko, Adv. Opt. Mater. 2015, 3, 280-320.
- [30] M. Kaur, D. H. Choi, Chem. Soc. Rev. 2015, 44, 58-77.
- [31] a) M. Stolte, S.-L. Suraru, P. Diemer, T. He, C. Burschka, U. Zschieschang, H. Klauk, F. Würthner, *Adv. Funct. Mater.* 2016, 26, 7415–7422; b) E. D. Głowacki, H. Coskun, M. A. Blood-Forsythe, U. Monkowius, L. Leonat, M. Grzybowski, D. Gryko, M. S. White, A. Aspuru-Guzik, N. S. Sariciftci, *Org. Electron.* 2014, *15*, 3521–3528.
- [32] W. Li, K. H. Hendriks, M. M. Wienk, R. A. J. Janssen, Acc. Chem. Res. 2016, 49, 78-85.
- [33] a) K. Praefcke, M. Jachmann, D. Blunk, M. Horn, *Liq. Cryst.* **1998**, 24, 153-156; b) Y. Zhou, C. X. Guzman, L. C. Helguero-Kelley, C. Liu, S. R. Peurifoy, B. Captain, A. B. Braunschweig, *J. Phys. Org. Chem.* **2016**, 29, 689-699.
- [34] a) J. S. Zambounis, Z. Hao, A. Iqbal, *Nature* 1997, 388, 131–132;
 b) S. N. Ivashevskaya, *Acta Crystallogr. Sect. E* 2017, 73, 507–510.
- [35] a) T. Kaiser, H. Wang, V. Stepanenko, F. Würthner, Angew. Chem. Int. Ed. 2007, 46, 5541-5544; Angew. Chem. 2007, 119, 5637-5640; b) S. Herbst, B. Soberats, P. Leowanawat, M. Lehmann, F. Würthner, Angew. Chem. Int. Ed. 2017, 56, 2162-2165; Angew. Chem. 2017, 129, 2194-2197.
- [36] G. M. Fischer, E. Daltrozzo, A. Zumbusch, Angew. Chem. Int. Ed. 2011, 50, 1406–1409; Angew. Chem. 2011, 123, 1442–1445.
- [37] R. van der Weegen, P. A. Korevaar, P. Voudouris, I. K. Voets, T. F. A. de Greef, J. A. J. M. Vekemans, E. W. Meijer, *Chem. Commun.* 2013, 49, 5532–5534.
- [38] a) X. Feng, W. Pisula, K. Müllen, J. Am. Chem. Soc. 2007, 129, 14116-14117; b) M. R. Hansen, T. Schnitzler, W. Pisula, R. Graf, K. Müllen, H. W. Spiess, Angew. Chem. Int. Ed. 2009, 48, 4621 4624; Angew. Chem. 2009, 121, 4691-4695.
- [39] M. Lehmann, M. Hügel, Angew. Chem. Int. Ed. 2015, 54, 4110– 4114; Angew. Chem. 2015, 127, 4183–4187.
- [40] Note that these two π - π -stacked DPP dimers are of mirror image configuration and thus in enantiomeric relation. Since the assembly is composed of alternate stacking of the dimers, it is necessarily achiral.
- [41] O. Sumner Makin, P. Sikorski, L. C. Serpell, J. Appl. Crystallogr. 2007, 40, 966–972.

Manuscript received: May 18, 2017 Accepted manuscript online: July 6, 2017 Version of record online:

www.angewandte.org

© 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Angew. Chem. Int. Ed. 2017, 56, 1-5

These are not the final page numbers!





Communications



Communications

Liquid Crystals

- B. Soberats,* M. Hecht,
- F. Würthner* _____

Diketopyrrolopyrrole Columnar Liquid-Crystalline Assembly Directed by Quadruple Hydrogen Bonds



A carefully designed diketopyrrolopyrrole dye self-assembles via quadruple hydrogen bonds into columnar liquid-crystalline phases. The 1D assembly is formed by the stack of two enantiomerically related dimers (A and B) with complementary hydrogen-bonding topology. As a result of this stacking mode, the dyes are oriented parallel to the columnar axis.

