

Amino acid derivatives of perylenediimide and their N–H···O peptide bond dipoles-templated solid state assembly into stacks†

Cyprien Lemouchi,^a Sergey Simonov,^{a,b} Leokadiya Zorina,^{a,b} Christelle Gautier,^a Piétrick Hudhomme^a and Patrick Batail^{*a}

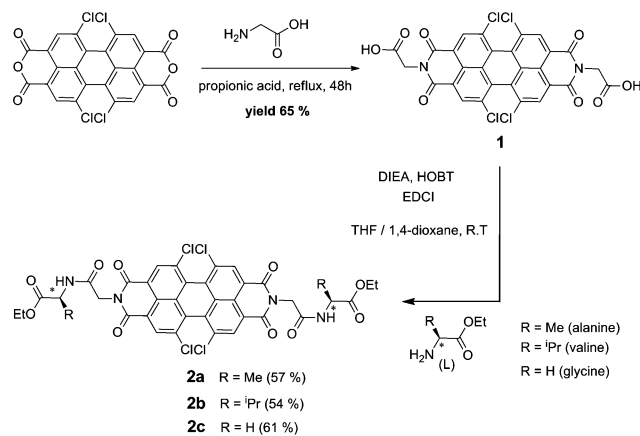
Received 20th July 2011, Accepted 1st September 2011

DOI: 10.1039/c1ob06213a

A methodology is proposed to provide direct access in good yields to peptide residues-appended perylenediimides PDI-(Cl₄)-[Gly-Ala(OEt)]₂, **2a**, PDI-(Cl₄)-[Gly-Val(OEt)]₂, **2b** and PDI-(Cl₄)-[Gly-Gly(OEt)]₂, **2c** from a generic perylenediimide (PDI) platform symmetrically functionalized with carboxylic acids at the imide sites, PDI-(Cl₄)-[Gly(OH)]₂, **1**. The latter is obtained in good purity by a non classical two-steps route avoiding the many, notoriously cumbersome successive chromatography steps typical of PDI chemistry, and including a single final purification allowing to crystallize the water soluble pure diacid **1**, of great interest in its own right for further developments in a variety of fields. Then, the synthesis, crystallization and analysis of the crystal structures of **2a** and **2b** reveal a common pattern of self-assembly of the outer peptide residues based on collections of parallel N–H···O peptidic hydrogen bonds running alongside stacks where the constraints imposed upon on the inner PDI skeletons by long range interaction of these parallel electric dipoles reduce the dihedral angles around the bay regions by as much as 11% down to 32°.

Introduction

The research reported here was designed as a materials-discovery initiative to explore the outcome of competing intermolecular hydrogen-bonding interactions^{1,2} in directing the structure of crystalline solids based on tetrachloro bay-substituted perylenediimide (PDI-(Cl₄)) cores^{3,4} whose both imide termini are functionalized by peptide residues,^{5,6} like PDI-(Cl₄)-[Gly-Ala(OEt)]₂, **2a**, PDI-(Cl₄)-[Gly-Val(OEt)]₂, **2b** and PDI-(Cl₄)-[Gly-Gly(OEt)]₂, **2c** (Scheme 1). This objective requires the synthesis of PDI-(Cl₄)-[Gly(OH)]₂, **1**, a dicarboxylic acid PDI of interest in its own right because of its expected solubility in water.^{6a,7} Our goal was to devise a system whereby the pattern of overlap within stacks of halogen-substituted, twisted π -conjugated skeletons with enhanced electron acceptor ability⁴ would be modulated as a result of the demand of the hydrogen bond donor/acceptor character of the outer peptide fragments. Our idea was that the structure-directing ability of peptide residues⁸ would stabilize⁹ long range ordered electric dipole interactions within large collections of intermolecular N–H···O peptidic bonds and template



Scheme 1

the formation of stacks, modulate the electrostatics of their environment, and, ultimately, the charge carriers mobility.^{9,10} Although the importance of electrostatic interactions in biology is intensely investigated,¹¹ for example in the context of the role of the environment on electron transfer in tetraheme cytochrome c where the chemical activity of a heme propionate becomes paramount,^{11a,b} a recent trend has emerged where their significance in tetrathiafulvalene-based materials chemistry and physics is explored with an emphasis on hydrogen bonded constructs.^{2,12,13} This approach, extended herein to peptide-substituted PDIs, is inspired by seminal work by Würthner and co-workers^{3,4,14–17} demonstrating the use of perylene-3,4,9,10-tetracarboxylic diimide derivatives

^aLaboratoire MOLTECH-Anjou, CNRS, University of Angers, 49045, Angers, France. E-mail: patrick.batail@univ-angers.fr

^bInstitute of Solid State Physics, Russian Academy of Sciences, 142432, Chernogolovka, MD, Russia

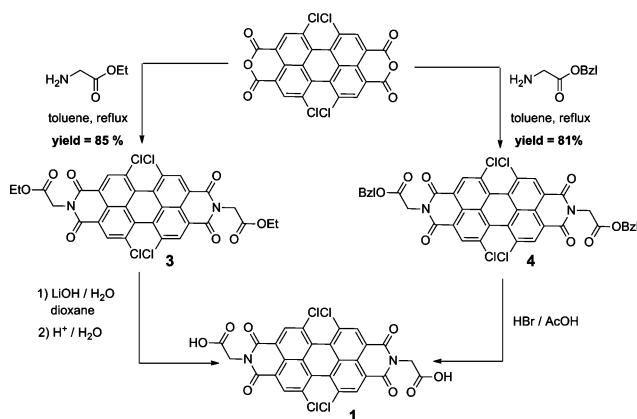
† Electronic supplementary information (ESI) available: UV-visible absorption spectra for **2a–c**; Cyclic voltammograms (CV) of compounds **2a** and **2b** and CV of **1**; Overlap modes for PDI-(Cl₄)-[C₂H₄OH][4-(*n*-C₅H₁₁)], PDI-(Cl₄)-[4-(*n*-C₁₂H₂₅)C₆H₄], **2a** and **2b**. CCDC reference numbers 833909 and 833910. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1ob06213a

as fluorophores for the construction of functional supramolecular architectures self assembled by metal coordination or by hydrogen bonding interactions into J-aggregates or gels. In that context, the series of compounds **2** reported here are seen as novel precursors of n-type semiconductors with potential prospects for applications in photovoltaic devices, organic field-effect transistors and light-emitting diodes.¹⁸ In that respect, a significant templating effect by long range intermolecular N–H···O peptidic bond dipoles interactions is shown here to affect the structure of the twisted PDI-(Cl₄) skeletons and stacks topology.

Results and discussion

The synthesis of a PDI dicarboxylic acid such as **1** is challenging because of several anticipated adverse factors like a lack of solubility, the presence of polar acid carboxylic functions, and a tendency to aggregate even at low concentrations. To prevent aggregation and enhance solubility, a proven strategy is to substitute the bay region by halides (Cl, Br) or amines, thereby imposing a torsion angle of about 36° to the perylene core.^{3,4,19} The tetrachloro-substituted PDI platform was also chosen to avoid conformational isomerism imposed by different orientations of tetraaryloxy substituents.

The synthesis of **1** typically involves a condensation reaction between 1,6,7,12-tetrachloro-3,4,9,10-tetracarboxylic dianhydride and an aliphatic amine carrying a protected carboxylic function, here an amino acid H₂N–CHR–CO₂H. PDI-(Cl₄)-[Gly(OH)]₂, **1** (R = H) was our prime target since bulkier R substituents have an adverse effect on crystallization²⁰ and favor the stabilization of liquid crystalline states instead.^{6d} In order to overcome the lack of solubility of any organic carboxylic acid a common practice is to protect the latter as soluble alkyl ester or benzyl ester derivatives that may be purified by chromatography. Subsequent deprotection under acid or basic conditions, like TFA, HBr/AcOH for *tert*-butyl ester or benzyl ester, or an alkali hydroxide (LiOH, KOH, NaOH) for ethyl ester, is well known to deliver diacid derivatives with a good purity. However, PDI-(Cl₄) cores remain sensitive to basic conditions and nucleophilic attacks at the bay region. Therefore, cleavage of the protecting group must take place under softer conditions, preventing the use of nucleophilic bases. With these prerequisites in mind, we synthesized PDI-(Cl₄)-[Gly(OEt)]₂, **3** and PDI-(Cl₄)-[Gly(OBzl)]₂, **4** by condensing H-Gly-OEt and H-Gly-OBzl²¹ onto 1,6,7,12-tetrachloro-3,4,9,10-tetracarboxylic dianhydride²² in good yields (Scheme 2). As anticipated, a complete deprotection of the ethyl ester required an excess of LiOH yielding in turn several by-products revealed on TLC-plates which could result from a decomposition of the PDI-(Cl₄)-core. Likewise, cleavage of the benzyl ester with HBr/AcOH²³ cannot be completed under soft conditions and higher acid concentrations resulted in side-reactions on the PDI-(Cl₄)-core. Therefore, as exemplified in Scheme 1, the reaction was carried out using 1,6,7,12-tetrachloro-3,4,9,10-tetracarboxylic dianhydride and the unprotected glycine in propionic acid at reflux for 48 h,²⁴ *via* a Nucleophilic Addition Ring-Opening Ring-Closing mechanism. This synthesis successfully delivers PDI-(Cl₄)-[Gly(OH)]₂, **1** in one step with the notable interest that this direct route meets the challenge of providing a reasonably pure dicarboxylic acid with the additional benefit of a desirable work up using successive



Scheme 2

washings only, that is, preventing the use of chromatography steps notoriously cumbersome in PDI chemistry. Note that the success of the methodology is the solubility of PDI-(Cl₄)-[Gly(OH)]₂, **1** in potassium carbonate aqueous solutions. Having reached that level of purity for **1**, independently of a further final purification step discussed below, the compound was engaged in a peptide coupling reaction (Scheme 1) following literature procedures^{5,8} to yield **2a** (57% yield) and **2b** (54% yield) as red powdered materials after purification by silica gel column chromatography. Finally, a single chromatography on silica gel completes the compound purification and delivers **1** in 65% yield with a good purity. **1** proved to be readily soluble in THF allowing for ¹H and ¹³C NMR characterization in THF-d₈. Single crystals of **1** are obtained by slow evaporation out of a THF solution; note, however, that the latter rapidly change into a crystalline powder preventing the determination of their structure by X-ray diffraction.

Slow diffusion of ether in dimethylformamide solutions^{9,25} of **2** affords needle-like single crystals of both compounds. Note that although these crystalline needles do not age well as they bent with time and their faces become opalescent, a drawback that precluded investigations of their transport properties, we were able to collect X-ray diffraction data and determine their crystal structures discussed below.

The electronic spectra for **1** and **2a–b** (Figure S1†) all show the three PDI characteristic bands at 427, 486 and 520 nm. Two reversible reduction waves were detected (Figures S2†) at –0.77 and –0.94 V and –0.79 and –0.97 V vs. Fc⁺/Fc for **2a** and **2b**, respectively, corresponding to the formation of radical anions and dianions with no evidence for a reversible oxidation process, as expected for tetrahalogeno-substituted PDI derivatives.⁴

Despite different crystal systems and space groups, the crystal structures of PDI-(Cl₄)-[Gly-Ala(OEt)]₂, **2a** (Fig. S3a†) and PDI-(Cl₄)-[Gly-Val(OEt)]₂, **2b** (Fig. S3b†) are remarkably similar. In both compounds, one identifies slabs of stacks of tetrachloro perylene diimide cores, the latter running along *a* in the triclinic and orthorhombic unit cells, respectively. Hence, the whole of the structural analysis comes down to a careful examination of the compared stack topologies shown in Fig. 1.

The salient, distinguishing feature of both solids is the identification of self-assembled strings of N–H···O hydrogen bonds. Here, their inherent electric dipoles²⁶ adopt a common, parallel orientation, cooperating to provide a robust template for the π -conjugated PDI-(Cl₄) cores within the stack. One feature stands

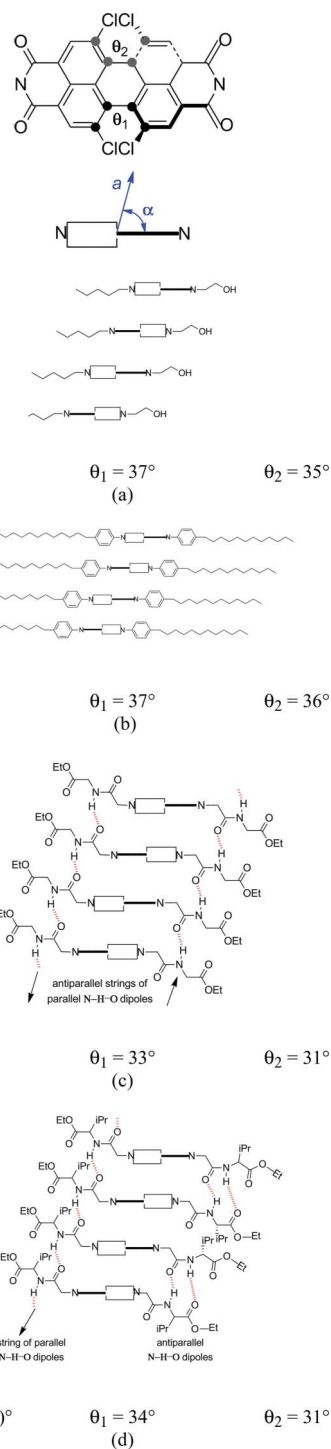
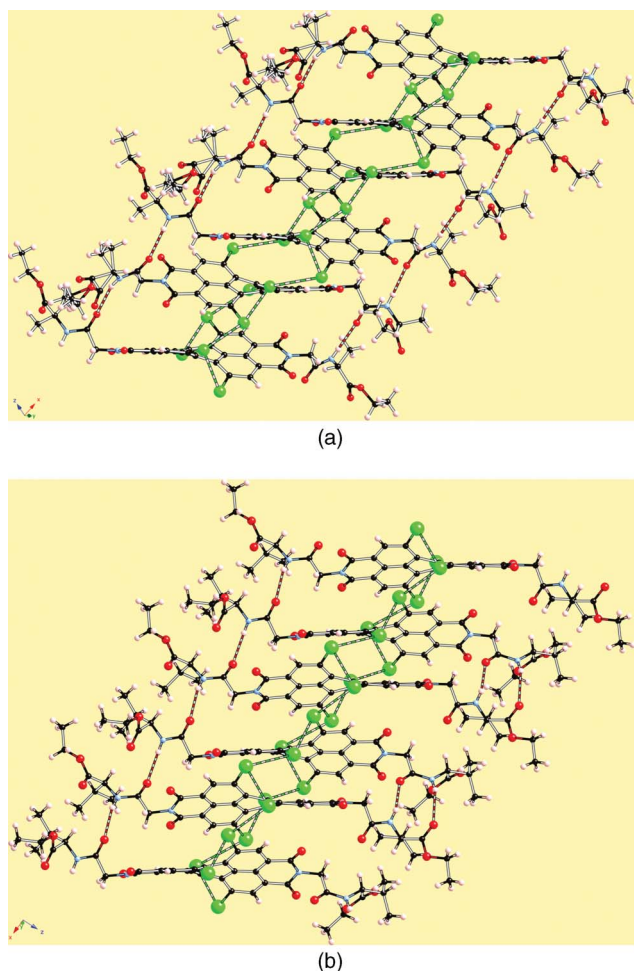


Fig. 1 A similar balance of N–H...O and Cl...Cl interactions templates the pattern of intermolecular overlap of the twisted PDI-(Cl₄) skeletons along the stacks in (a) **2a** and (b) **2b**. In both compounds the stacks consist of alternating two independent molecules. **2a**: N...O distances²⁶ are in the range 2.96(1)–3.03(1) Å; intra and inter Cl...Cl PDI-(Cl₄) skeleton distances are 2.945(3)–3.102(3) Å and 3.631(3)–3.835(3) Å, respectively. **2b**: N...O distances in the infinite string on the left are 3.040(9) and 3.087(8) Å; antiparallel N...O distances in the dimeric units on the right are a short 2.827(8)^{26a} and 3.281(8)^{26b} Å. Intra and inter Cl...Cl PDI-(Cl₄) skeleton distances are 2.973(2)–3.095(2) Å and 3.467(2)–3.903(2) Å, respectively.

out though and differentiates the templating patterns between **2a** and **2b** (Fig. 1): while identical antiparallel strings of parallel N–H...O dipoles run on both sides of any stack in **2a** (Fig. 1a), one string of similar parallel N–H...O dipoles runs on the left-hand side of the stack in **2b** (Fig. 1b) when successive dimers of antiparallel N–H...O dipoles are stabilized on its right hand side.

Further insight on the strength of the templating effect exerted upon the stack topology and inner PDI-(Cl₄) skeletons configuration by the self-assembly of the outer peptides residues is gained by comparing in Fig. 2 a set of two stack characteristics for **2a** and **2b**, namely the angle α between the stacking axis a and the PDI intramolecular N–N axis (note that the shift normal to N–N is identical for all four compounds, as shown in Figure S4†), and the dihedral angles θ_1 and θ_2 , with those for two other compounds, PDI-(Cl₄)-[C₂H₄OH][4-(*n*-C₅H₁₁)]¹⁹ and PDI-(Cl₄)-[4-(*n*-C₁₂H₂₅)C₆H₄]⁴ for which these characteristics

Fig. 2 Evolution of the angle α and dihedral angles θ_1 and θ_2 (between carbon atoms marked with solid dots) from (a) PDI-(Cl₄)-[C₂H₄OH][4-(*n*-C₅H₁₁)]¹⁹ to (b) PDI-(Cl₄)-[4-(*n*-C₁₂H₂₅)C₆H₄]⁴ to (c) PDI-(Cl₄)-[Gly-Ala(OEt)]₂, **2a** where θ_1 are 32(2)° and 34(2)° and θ_2 are 30(2)° and 32(1)°; and (d) PDI-(Cl₄)-[Gly-Val(OEt)]₂, **2b** where θ_1 are 36(1) and 32(1)°, θ_2 are 31(1) and 31(1)°.

(Fig. 2a and 2b) are quite similar. A significant discontinuity is registered as α and θ for **2a** (Fig. 2c) and **2b** (Fig. 2d), whose averaged values are 53° Å and 32°, changes by 20% and –11%, respectively, from the reference compounds,

PDI-(Cl₄)-[C₂H₄OH][4-(*n*-C₅H₁₁)] and PDI-(Cl₄)-[4-(*n*-C₁₂H₂₅)C₆H₄] with softer templates. This illustrates a significant increase of constraints qualifying a discontinuity in a series where long range electrostatic stabilization of large collections of parallel N-H...O peptidic bond dipoles imposes a harder templating effect upon the inner, π-conjugated PDI-(Cl₄) cores along the stacks.

Conclusions

The aforementioned results demonstrate that the self-assembly of outer peptide residues attached to PDI-(Cl₄) skeletons is directed by electrostatic stabilization of large collections of parallel N-H...O peptidic bond dipoles. A clear and distinctive influence, and exquisite level of control, of the peptide residues over two structural parameters, the lateral shift and curvature of the PDI-cores along the stacks, is expressed in the angles α and dihedral angles θ, characteristic of a tandem-modal self-assembly in the crystalline solid state. We are now applying the synthetic methodology reported herein to the preparation of novel series of peptidic PDIs with the objective to engage their anionic carboxylate forms in conducting crystalline radical cation salts,^{9,10} to tailor precursors of bulk, self-assembled crystalline frameworks²⁷ or molecular layers at metal surfaces;^{27a,c,e} as well as for applications in photovoltaic devices, organic field-effect transistors and light-emitting diodes,^{3,4,14-18} where a modulation of the electronic structure upon peptide-driven⁶ self-assembly need to be investigated further.

Experimental section

Synthesis of PDI-(Cl₄)-[CH₂-CO₂H]₂ or PDI-(Cl₄)-[Gly(OH)]₂, **1**

Glycine (3 g, 40 mmol) was added to a solution of 1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylic dianhydride (BASF)²² (3 g, 5.68 mmol) in propionic acid (50 mL). The reaction mixture was heated under reflux for 48h. After cooling, the reaction mixture was poured into a 50 : 50 mixture of THF and saturated NH₄Cl aqueous solution. Following a first extraction, the isolated red THF layer was poured into of saturated K₂CO₃ aqueous solution; gas evolved from the solution, the red-colored water layer was extracted with THF (2 × 50 mL). Then, 100 mL of THF were added under stirring to the former and the mixture was acidified upon adding dropwise a 6 N HCl solution to reach a pH of 3, by which a red coloration of the organic layer and a total discoloration of the water layer took place. The mixture was then stirred for 20 min and extracted. The THF layer isolated by extraction was evaporated to dryness under reduced pressure. The red solid **1** was washed successively with water (2 × 50 mL) and Et₂O (3 × 50 mL) and dried overnight. The solid residue was purified by column chromatography on silica gel using a 90/10 CH₂Cl₂/acetic acid mixture as eluent. A red powder (2.4 g, 65%) was isolated. DSC: T_{dec.}: 267 °C; ¹H NMR (THF-d₈, 300 MHz) δ 8.71 (s, 4H), 3.63 (s, 4H); the signal for the COOH proton was too broad to be correctly described; ¹³C NMR (THF-d₈, 300 MHz) δ 169.6, 163.0, 136.5, 133.8, 133.1 130.2, 125.0, 42.4; MALDI-Tof calcd for C₂₈H₁₀Cl₄N₂O₈: 641.92; found 641.9. Anal. Calcd. for: C, 52.20; H, 1.56; N, 4.35. Found: C, 51.64; H, 2.03; N, 3.89.

Synthesis of PDI-(Cl₄)-[Gly-Ala(OEt)]₂, **2a**

EDCI (197 mg, 1.03 mmol) then (L)-H-Ala-OEt, HCl (158 mg, 1.03 mmol) were successively added to a THF (40 mL) and 1,4-dioxane (10 mL) mixture containing **1** (300 mg, 0.47 mmol), DIEA (0.6 mL) and HOBT (139 mg, 1.03 mmol). The reaction mixture was stirred at room temperature for 48 h and TLC monitored (eluent: CH₂Cl₂ + 10% AcOH). The reaction mixture was poured into 100 mL of CH₂Cl₂; the solution was washed with aqueous NaHCO₃ and H₂O. The organic layer was dried over MgSO₄, filtered and evaporated under reduced pressure. The red solid residue was purified by column chromatography on silica gel using a mixture 90/10 CH₂Cl₂/acetic acid solutions as the eluent. **2a** is obtained as a red solid (225 mg, 57%) and it was crystallized by slow diffusion liq/liq. of Et₂O in a solution of **2a** dissolved in DMF.

DSC: T_{dec.} = 312 °C; ¹H NMR (CDCl₃, 300 MHz) δ 8.63 (4H, s), 6.66 (2H, d, J = 7.5 Hz), 4.91 (4H, m), 4.63 (2H, q₁d₂, J₁ = 7.5 Hz, J₂ = 7.5 Hz), 4.23 (4H, q, J = 7.5 Hz), 1.47 (6H, d, J = 7.5 Hz), 1.29 (6H, t, J = 7.5 Hz); ¹³C NMR (CDCl₃, 300 MHz) δ 172.9, 165.6, 162.0, 135.4, 133.2, 131.4, 128.8, 122.8, 61.7, 48.5, 42.9, 18.6, 14.1; MALDI-TOF (pos. mode) calcd for [C₃₈H₂₈Cl₄N₄O₁₀]⁺: 840.1; found 840.1.

Synthesis of PDI-(Cl₄)-[Gly-Val(OEt)]₂, **2b**

The synthetic procedure for **2a** was applied using (L)-H-Val-OEt, HCl. **2b** is obtained as a red solid (227 mg, 54%); it is crystallized by slow diffusion liq/liq. of an Et₂O solution of **2b** in DMF. DSC: T_{decomp.} = 337 °C; ¹H NMR (CD₂Cl₂, 300 MHz) δ 8.61 (s, 4H), 6.63 (d, 2H, J = 7.5 Hz), 4.90 (m, 4H), 4.56 (m, 2H), 4.22 (m, 4H), 2.19 (oct, 2H, J = 7 Hz), 1.29 (t, 6H, J = 7.5 Hz), 0.97 (t, 12H, J = 7 Hz); ¹³C NMR (CD₂Cl₂, 300 MHz) δ 172.1, 166.6, 162.3, 135.7, 133.3, 131.8, 129.2, 123.8, 123.2, 61.8, 57.8, 43.3, 32.0, 19.1, 18.0, 14.4; MALDI-TOF (pos. mode) calcd for [C₄₂H₃₆Cl₄N₄O₁₀ + H]⁺: 897.1; found 896.9. Anal. Calcd. for: C, 56.14; H, 4.04; N, 6.24. Found: C, 55.65; H, 3.94; N, 6.24.

Synthesis of PDI-(Cl₄)-[Gly-Gly(OEt)]₂, **2c**

The synthetic procedure for **2a** was applied using H-Gly-OEt, HCl. **2c** is obtained as a red solid (233 mg, 61%). T_{decomp.} = 300 °C. ¹H NMR (CD₂Cl₂, 300 MHz) δ 8.68 (s, 4H), 6.36 (t, 2H, J = 7 Hz), 4.92 (s, 4H), 4.23 (q, 4H, J = 7 Hz), 4.07 (d, 4H, J = 7 Hz), 1.27 (t, 6H, J = 7 Hz); ¹³C NMR (CD₂Cl₂, 300 MHz) δ 169.9, 166.7, 162.5, 135.8, 133.4, 123.2, 62.0, 41.9, 30.1, 14.3; MALDI-TOF (pos. mode) calcd for [C₃₆H₂₄Cl₄N₄O₁₀ + H]⁺: 813.0; found 812.8.

Synthesis of PDI-(Cl₄)-[CH₂-CO₂Et]₂ or PDI-(Cl₄)-[Gly(OEt)]₂, **3**

Glycine ethyl ester hydrochloride (578 mg, 4.16 mmol) was added to a solution of 1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylic dianhydride²² (1 g, 1.89 mmol) in toluene (50 mL). The reaction mixture was heated under reflux for 24h. After cooling, the reaction mixture was evaporated to dryness under low pressure. The collected red solid was purified by silica gel column chromatography with dichloromethane as eluent. A red powder (1.1 g, 85%) was obtained. DSC: an exothermic peak at 290 °C signals a phase transition prior to the decomposition at T_{dec.} = 312 °C; ¹H NMR (CD₂Cl₂, 300 MHz) δ 8.7 (s, 4H), 4.94

(s, 4H), 4.25 (q, 4H, $J = 7.5$ Hz), 1.31 (t, 6H, $J = 7.5$ Hz); ^{13}C NMR (CD_2Cl_2 , 300 MHz) δ 167.9, 162.3, 135.8, 133.4, 131.9, 129.4, 123.2, 62.2, 42.0, 14.4; MALDI-TOF (pos. mode) calcd for $[\text{C}_{32}\text{H}_{18}\text{Cl}_4\text{N}_2\text{O}_8]^+$: 698; found 697.9.

Synthesis of PDI-(Cl₄)-[Gly(OBzl)]₂, 4

4 was prepared from 1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylic dianhydride²² (1 g, 1.89 mmol) and Glycine benzyl ester trifluoroacetic salt²¹ ((1.2 g, 4.15 mmol) following the procedure for **3**. **4** is isolated as a red solid (1.3 g, 81%). DSC: $T_{\text{dec.}} = 322$ °C; ^1H NMR (CD_2Cl_2 , 300 MHz) δ 8.71 (s, 4H), 7.38 (m, 10H), 5.24 (s, 4H), 5.02 (s, 4H); ^{13}C NMR (CD_2Cl_2 , 300 MHz) δ 167.9, 162.3, 135.8, 133.5, 129.5, 129.0, 128.8, 128.5, 123.2, 67.8, 42.0; MALDI-TOF (pos. mode) calcd for $[\text{C}_{42}\text{H}_{22}\text{Cl}_4\text{N}_2\text{O}_8 + \text{H}]^+$: 823.0; found 823.0. Anal. Calcd. for: C, 61.19; H, 2.69; N, 3.40. Found: C, 60.04; H, 2.83; N, 3.13.

X-Ray structure analysis

2a: $\text{C}_{38}\text{H}_{28}\text{Cl}_4\text{N}_4\text{O}_{10}$, $M = 842.44$, $T = 150(1)\text{K}$, triclinic, $P1$, $a = 9.978(3)$, $b = 10.704(3)$, $c = 17.817(6)$ Å, $\alpha = 74.10(2)$, $\beta = 81.31(2)$, $\gamma = 81.28(2)^\circ$, $V = 1796.9(9)$ Å³, $Z = 2$, $D_c = 1.557$ g cm⁻³, $\mu = 3.97$ cm⁻¹, $F(000) = 864$, $2\Theta_{\text{max}} = 56.0^\circ$, reflections measured 16721, unique reflections 11506 ($R_{\text{int}} = 0.0668$), reflections with $I > 2\sigma(I) = 6817$, parameters refined 885, $R_1 = 0.0713$, $wR_2 = 0.1169$, GOF = 1.015. **2b**: $\text{C}_{42}\text{H}_{36}\text{Cl}_4\text{N}_4\text{O}_{10}$, $M = 898.55$, $T = 150(1)\text{K}$, orthorhombic, $P2_12_12_1$, $a = 10.019(2)$, $b = 16.372(3)$, $c = 49.573(9)$ Å, $V = 8132(3)$ Å³, $Z = 8$, $D_c = 1.468$ g cm⁻³, $\mu = 3.56$ cm⁻¹, $F(000) = 3712$, $2\Theta_{\text{max}} = 52.1^\circ$, reflections measured 44150, unique reflections 11623 ($R_{\text{int}} = 0.0686$), reflections with $I > 2\sigma(I) = 7584$, parameters refined 1095, $R_1 = 0.0642$, $wR_2 = 0.1241$, GOF = 1.036. Single crystal X-ray diffraction data were collected at 150 K using a Bruker Nonius KappaCCD diffractometer with monochromatized Mo-K α -radiation ($\lambda = 0.71073$ Å, graphite monochromator, combined ϕ/ω -scans). Empirical absorption correction of experimental intensities was applied using the SADABS program.²⁸ The structures were solved by a direct method followed by Fourier syntheses and refined by a full-matrix least-squares method using the SHELX-97 programs.²⁹ All non-hydrogen atoms were refined in an anisotropic approximation. H-atoms were placed in idealized positions and refined using a riding model, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. CCDC 833909 and 833910 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Notes and references

- (a) Supramolecular assemblies based on hydrogen bonds: G. R. Desiraju and T. Steiner, *The Weak Hydrogen Bond*, Oxford University Press, New York, 1999; (b) M. Alajarin, A. E. Aliev, A. D. Burrows, K. D. M. Harris, A. Pastor, J. W. Steed and D. R. Turner, *Supramolecular Assembly via Hydrogen Bonds I, Structure and Bonding*, Vol. 108, ed. D. M. P. Mingos, Springer-Verlag, Berlin, 2004; (c) G. R. Desiraju, *Chem. Commun.*, 2005, 2995; (d) G. R. Desiraju, *Angew. Chem., Int. Ed.*, 2007, **46**, 8342; (e) G. Gilli and P. Gilli, *The nature of the hydrogen bond: Outline of a comprehensive hydrogen bond theory*, Oxford University Press, New York, 2009.
- Hydrogen bonding in π -type, TTF-based systems: M. Fourmigué and P. Batail, *Chem. Rev.*, 2004, **104**, 5379.

- (a) F. Würthner and M. Stolte, *Chem. Commun.*, 2011, **47**, 5109; (b) F. Würthner, *Chem. Commun.*, 2004, 1564.
- Z. Chen, M. G. Debye, T. Debaerdemaeker, P. Osswald and F. Würthner, *ChemPhysChem*, 2004, **5**, 137.
- R. Behrendt, M. Schenk, H.-J. Musiol and L. Moroder, *J. Pept. Sci.*, 1999, **5**, 519.
- There is a current strong interest in the chemistry of perylene diimide-carboxylics, especially of peptide carboxylic-substituted PBI's: (a) F. Yukruk, A. L. Dogan, H. Canpinar, D. Guc and E. U. Akkaya, *Org. Lett.*, 2005, **7**, 2885; (b) O. Ozcan, F. Yukruk, E. U. Akkaya and D. Uner, *Appl. Catal., B*, 2007, **71**, 291; (c) E. Mete, D. Uner, M. Cakmak, O. Gülsüren and S. Ellialtıoglu, *J. Phys. Chem. C*, 2007, **111**, 7539; (d) Y. Xu, S. Leng, C. Xue, R. Sun, J. Pan, J. Ford and S. Jin, *Angew. Chem., Int. Ed.*, 2007, **46**, 3896; (e) D. Kahir, O. Gülsüren, E. Mete and S. Ellialtıoglu, *J. Phys. Chem. C*, 2011, **115**, 9220.
- (a) H. Y. Au-Yeung, P. Pengo, G. Dan Pantos, S. Otto and J. K. M. Sanders, *Chem. Commun.*, 2009, 419; (b) B. M. Bulheller, G. Dan Pantos, J. K. M. Sanders and J. D. Hirst, *Phys. Chem. Chem. Phys.*, 2009, **11**, 6017; (c) F. B. L. Cougnon, H. Y. Au-Yeung, G. Dan Pantos and J. K. M. Sanders, *J. Am. Chem. Soc.*, 2011, **133**, 3198.
- Y. Li, G. Li, X. Wang, W. Li, Z. Su, Y. Zhang and Y. Ju, *Chem.–Eur. J.*, 2009, **15**, 6399.
- A. El-Ghayoury, C. Mézière, S. Simonov, L. Zorina, M. Cobián, E. Canadell, C. Rovira, B. Náfrádi, B. Sipos, L. Forró and P. Batail, *Chem.–Eur. J.*, 2010, **16**, 14051.
- (a) L. Zorina, S. Simonov, C. Mézière, E. Canadell, S. Suh, S. E. Brown, P. Foury-Leylekian, P. Fertey, P. Pouget and P. Batail, *J. Mater. Chem.*, 2009, **19**, 6980; (b) Y. Lakhdar, C. Mézière, L. Zorina, M. Giffard, P. Batail, E. Canadell, P. Auban-Senzier, C. Pasquier, D. Jérôme, B. Náfrádi and L. Forró, *J. Mater. Chem.*, 2011, **21**, 1516.
- The importance of electrostatics in biology: (a) H. Akutsu and Y. Takayama, *Acc. Chem. Res.*, 2007, **40**, 171; (b) G. Bränden, M. Bränden, B. Schmidt, D. A. Mills, S. Ferguson-Miller and P. Brzezinski, *Biochemistry*, 2005, **44**, 10466; (c) R. N. Barnett, C. L. Cleveland, A. Joy, U. Landman and G. B. Schuster, *Science*, 2001, **294**, 567; (d) M. E. Davis and J. A. McCammon, *Chem. Rev.*, 1990, **90**, 509; K. Harada, M. Makino, H. Sugimoto, S. Hirota, T. Matsuo, Y. Shiro, Y. Hisaeda and T. Hayashi, *Biochemistry*, 2007, **46**, 9406; (e) F. C. Grozema, S. Tonzani, Y. A. Berlin, G. C. Schatz, L. D. A. Siebbeles and M. A. Ratner, *J. Am. Chem. Soc.*, 2008, **130**, 5157; (f) I. Levental, A. Cebers and P. A. Janmey, *J. Am. Chem. Soc.*, 2008, **130**, 9025; (g) J. E. Goldberger, E. J. Berns, R. Bitton, C. J. Newcomb and S. I. Stupp, *Angew. Chem., Int. Ed.*, 2011, **50**, 6292.
- (a) T. Murata, Y. Morita, K. Fukui, K. Sato, D. Shiomi, T. Takui, M. Maesato, H. Yamochi, G. Saito and K. Nakasuji, *Angew. Chem., Int. Ed.*, 2004, **43**, 6343; (b) T. Murata, Y. Morita, Y. Yakiyama, Y. Nishimura, T. Ise, D. Shiomi, K. Sato, T. Takui and K. Nakasuji, *Chem. Commun.*, 2007, 4009; (c) Y. Morita, E. Miyazaki, K. Fukui, S. Maki and K. Nakasuji, *Bull. Chem. Soc. Jpn.*, 2005, **78**, 2014; (d) E. Miyazaki, Y. Morita, Y. Yakiyama, S. Maki, Y. Umemoto, M. Ohmoto and K. Nakasuji, *Chem. Lett.*, 2007, **36**, 1102; (e) T. Murata, Y. Morita, Y. Yakiyama, K. Fukui, H. Yamochi, G. Saito and K. Nakasuji, *J. Am. Chem. Soc.*, 2007, **129**, 10837; (f) Y. Morita, Y. Yamamoto, Y. Yakiyama, T. Murata and K. Nakasuji, *Chem. Lett.*, 2008, **37**, 24; (g) T. Murata, Y. Yakiyama, K. Nakasuji and Y. Murata, *CrystEngComm*, 2011, **13**, 3689.
- (a) P. Blanchard, K. Boubekeur, M. Sallé, G. Duguay, M. Jubault, A. Gorgues, J. D. Martin, E. Canadell, P. Aubansenzier, D. Jérôme and P. Batail, *Adv. Mater.*, 1992, **4**, 579; (b) A. Penicaud, K. Boubekeur, P. Batail, E. Canadell, P. Auban-Senzier and D. Jérôme, *J. Am. Chem. Soc.*, 1993, **115**, 4101; (c) A. Dolbecq, M. Fourmigué, P. Batail and C. Coulon, *Chem. Mater.*, 1994, **6**, 1413; (d) A. Dolbecq, M. Fourmigué, F. C. Krebs, P. Batail, E. Canadell, R. Clerac and C. Coulon, *Chem.–Eur. J.*, 1996, **2**, 1275; (e) K. Boubekeur, R. Riccardi, P. Batail and E. Canadell, *C. R. Acad. Sci.*, 1998, **1**, 627; (f) A. Dolbecq, A. Guirauden, M. Fourmigué, K. Boubekeur, P. Batail, M. M. Rohmer, W. Benard, C. Coulon, M. Sallé and P. Blanchard, *J. Chem. Soc., Dalton Trans.*, 1999, 1241; (g) K. Heuzé, M. Fourmigué, P. Batail, E. Canadell and P. Auban-Senzier, *Chem.–Eur. J.*, 1999, **5**, 2971; (h) K. Heuzé, C. Mézière, M. Fourmigué, P. Batail, C. Coulon, E. Canadell, P. Auban-Senzier and D. Jérôme, *Chem. Mater.*, 2000, **12**, 1898; (i) A. Deluzet, R. Rousseau, C. Guilbaud, I. Granger, K. Boubekeur, P. Batail, E. Canadell, P. Auban-Senzier and D. Jérôme, *Chem.–Eur. J.*, 2002, **8**, 3884; (j) S. A. Baudron, P. Batail, C. Rovira, E. Canadell and R. Clérac, *Chem. Commun.*, 2003, 1820; (k) S. A. Baudron, N. Avarvari, P. Batail, C. Coulon, R. Clérac, E.

- Canadell and P. Auban-Senzier, *J. Am. Chem. Soc.*, 2003, **125**, 11583; (l) S. A. Baudron, N. Avarvari, E. Canadell, P. Auban-Senzier and P. Batail, *Chem.–Eur. J.*, 2004, **10**, 4498; (m) S. A. Baudron, P. Batail, C. Coulon, R. Clérac, E. Canadell, V. Laukhin, R. Melzi, P. Wzietek, D. Jérôme, P. Auban-Senzier and S. Ravy, *J. Am. Chem. Soc.*, 2005, **127**, 11785.
- 14 F. Würthner, *Pure Appl. Chem.*, 2006, **78**, 2341.
- 15 (a) F. Würthner and A. Sautter, *Chem. Commun.*, 2000, 445; (b) F. Würthner, A. Sautter, D. Schmid and P. J. A. Weber, *Chem.–Eur. J.*, 2001, **7**, 894.
- 16 T. E. Kaiser, H. Wang, V. Stepanenko and F. Würthner, *Angew. Chem., Int. Ed.*, 2007, **46**, 5541.
- 17 F. Würthner, B. Hanke and M. S. Harms, *Org. Lett.*, 2005, **7**, 967.
- 18 (a) C. Huang, S. Barlow and S. R. Marder, *J. Org. Chem.*, 2011, **76**, 2386; (b) D. Ke, C. Zhan, S. Xu, X. Ding, A. Peng, J. Sun, S. He, A. D. Q. Li and J. Yao, *J. Am. Chem. Soc.*, 2011, **133**, 11022.
- 19 S. Leroy-Lhez, J. Baffreau, L. Perrin, E. Levillain, M. Allain, M.-J. Blesa and P. Hudhomme, *J. Org. Chem.*, 2005, **70**, 6313.
- 20 (a) D. Dotcheva, M. Klapper and K. Mullen, *Macromol. Chem. Phys.*, 1994, **195**, 1905; (b) F. Würthner, C. Thalacker and A. Sautter, *Adv. Mater.*, 1999, **11**, 754.
- 21 P. Brough, C. K. Klumpp, A. Bianco, S. Campidelli and M. Prato, *J. Org. Chem.*, 2006, **71**, 2014.
- 22 We thank BASF-AG, Ludwigshafen, for providing 1,6,7,12-tetrachloroperylene tetracarboxylic dianhydride.
- 23 C. Gilvarg and Y. Levin, *J. Biological Chem.*, 1972, **247**, 543.
- 24 (a) F. Würthner, A. Sautter and J. Schilling, *J. Org. Chem.*, 2002, **67**, 3037; (b) W. Qiu, S. Chen, X. Sun, Y. Liu and D. Zhu, *Org. Lett.*, 2006, **8**, 867.
- 25 We thank A. El-Ghayoury for valuable insights on the crystallization of **2**.
- 26 (a) A supramolecular motif providing for the long range electrostatic stabilization of the α -helix (where N \cdots O is 2.86 Å), see: T. E. Creighton, in *Proteins, Structures and Molecular Properties*, W. H. Freeman, Ed., New York, 1993, p. 182; (b) S. R. Beeren and J. K. M. Sanders, *J. Am. Chem. Soc.*, 2011, **133**, 3804.
- 27 (a) A. G. Slater (née Phillips), P. H. Beton and Neil R. Champness, *Chem. Sci.*, 2011, **2**, 1440; (b) T. W. Chamberlain, E. S. Davies, A. N. Khlobystov and N. R. Champness, *Chem.–Eur. J.*, 2011, **17**, 3759; (c) J. C. Russell, M. O. Blunt, G. Goretzki, A. G. Phillips, N. R. Champness and Peter H. Beton, *Langmuir*, 2010, **26**, 3972; (d) C. B. Aakeroy, N. R. Champness and Christoph Janiak, *CrystEngComm*, 2010, **12**, 22; (e) L. Bartels, *Nat. Chem.*, 2010, **2**, 87.
- 28 R. Herbst-Irmer and G. M. Sheldrick, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1998, **B54**, 443.
- 29 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **A64**, 112.