Supporting Information of the Paper:

Supramolecular ordering of difuryldiketopyrrolopyrrole: the effect of alkyl chains and inter-ring twisting

Chaoying Fu,[a] Francine Bélanger-Gariépy,[b] Dmitrii F. Perepichka*,[a]

[a]Department of Chemistry and Center for Self-Assembled Chemical Structures, McGill University, 801 Sherbrooke Street West, Montréal, Quebec, Canada H3A 0B8. *dmtrii.perepichka@mcgill.ca
[b]Departement de Chimie, Universite de Montreal, Montreal, QC, Canada, H3T 1J4

Synthesis of 3,6-di(furan-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (DFDPP). The synthesis of DFDPP followed the reported procedures.[1] The yield was 84% and the spectroscopic analysis was idential to that of the reported sample. ^{1}H NMR (400 MHz, DMSO): δ 11.17 (s, 2H), 8.04 (d , J = 0.7 Hz, 2H), 7.64 (d, J = 1.8 Hz, 2H), 6.82 (dd, J = 1.8 Hz, 0.7 Hz, 2H).

Synthesis of DFDPP-C_{14}. DFDPP (0.50 g, 1.86 mmol) was mixed with K_2CO_3 (0.90 g, 6.51 mmol) in 10mL of dry DMF. 1-Bromotetradecane (1.55 g, 5.59 mmol) in 10mL dry DMF was added gradually and the reaction mixture was heated at 110ºC overnight. The reaction mixture was cooled to room temperature, diluted with water, and the organic phase was extracted with dichloromethane. The organic phase was dried over magnesium sulfate, producing, after evaporating the solvent, the crude product which was purified by silica gel column chromatography, eluting with 1:3 ethylacetate/hexane. The pure DFDPP-C_{14} was obtained as a dark red solid (0.662 g, 54 %). The spectroscopic analysis was idential to that of the reported sample.[2] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.30 (d, J = 1.8 Hz, 2H), 7.64 (d, J = 0.6 Hz, 2H), 6.70 (dd, J = 2 Hz, 0.6 Hz, 2H), 4.10 (t, J = 7.2 Hz, 4H), 1.68 (m, 4H), 1.36-1.24 (m, 22H), 0.88 (t, J = 5.2 Hz, 6H).

Synthesis of DFDPP-C_6. was prepared by the same procedure described above to yield pure product as golden shine needles (0.130 g, 40%). The spectroscopic analysis was idential to that of the reported sample.[3] ^{1}H NMR ($CDCl_3$, 400 MHz): δ8.30 (d, J = 1.6 Hz, 2H), 7.64 (d, J = 0.6 Hz, 2H), 6.70 (dd, J = 1.6 Hz, 0.6 Hz, 2H), 4.11 (t, J = 7.2 Hz, 4H), 1.69 (m, 4H), 1.39-1.30 (m, 12H), 0.88 (t, J = 6.4 Hz, 6H).

STM Measurement

STM experiments were carried out on a Nanoscope Multimode 8 (Bruker, Santa Barbara) under ambient pressure and at room temperature. Mechanically cut 80/20 Pt/Ir wire was used as the STM tip. All DFDPP-Cn (n = 6,14) solutions were made at a concentration of 0.1mM in n-tetradecane (98%, TCI) for STM experiments. Molecular monolayers were prepared by applying a drop of solution on graphite surface (SFR, XYZ grade); then, STM images were scanned at constant current mode and negative tip biases with respect to the samples. All the raw images were processed from WSxM.[4] The periodicities of lamellar networks of DFDPP-Cn were calibrated against the underlying graphite lattice obtained at lower bias voltage. All the molecular models were built in HyperChem 7.52[5] and the single molecular calculations were carried out by DFT at M06-2X/6-31 G (d) using the Gaussian 09 software.[6]

X-ray Crystallography

Suitable crystals of DFDPP-C_{14} and DFDPP-C_6 were selected, set on a Cryoloop and mounted on a Bruker Venture Metaljet diffractometer. The crystals were kept at 105 K during data collection. Using Olex2[7], the structures were solved with the ShelXT[8] structure solution program using Direct Methods and refined with the XL [9] refinement package using Least Squares minimisation. Crystallographic data have been deposited at Cambridge Crystallographic Data Centre (CCDC). Deposition numbers are CCDC 1440140 for DFDPP-C_6 and CCDC 1440141 for DFDPP-C_{14} (copies of data can be obtained via http://www.ccdc.cam.ac.uk/conts/retrieving.html).

DFT calculation

DFT calculations were performed with Gaussian 09. M06-2X functional[10,11] with the 6-31G(d) basis set was used to account for van der Waals interactions between DFDPP molecules. Calculations were done on isolated molecules and small clusters.

Dialkylated DFDPP, DTDPP and DPDPP molecules were optimized by single molecular calculations in gas phase. To reduce the computation cost, the alkyl chains were minimized into ethyl groups, which still contains the steric between amide oxygen of the DPP core and β-CH_2 group of the alkyl chain. Important features of the optimized molecular structures are summarized in Table S1. The calculations of ring twisting potentials of the three molecules were carried out on the above optimized structures. The single molecular energies were scanned when one of the rings was rotated from the optimized conformation to ca. 90° at 5° interval (see the energy plot in Fig.1a). A similar method was applied to calculate the alkyl chain torsion energy. Single molecular energies were scanned when one of the ethyl chains was rotated from 0° to 180° at 5° interval (C-C-N-C bond torsion, Fig. 1b).

A methyl-substituted DFDPP-Me model was used for the cluster calculation of DFDPP-C_6 self-assembly. A supramolecular cluster (containing 4 close-packed DFDPP-Me model molecules) was constructed according to the experimental unit cell parameters. During the optimization process, a plane symmetry Cs was imposed on the cluster, which allowed the four molecules to relax only in-plane so as to mimic the on-surface self-assembly. Total binding energy per molecule (E_b) within the 2D network is computed below. Based on the optimized cluster structure, we partition the intermolecular interactions into furyl…furyl electrostatic ($E_{F\cdots F}$) and furyl H…amide O (E_{hb}) weak H bonding interactions, which can be calculated in a similar method as E_b.

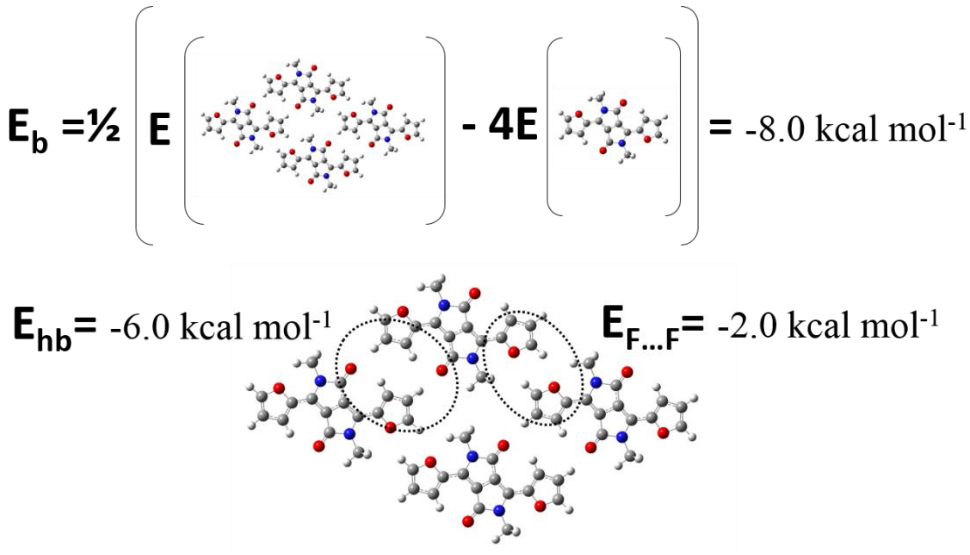

Table S1 Structural characteristics of the three DFT optimized (M06-2X/6-31G(d)) DPP derivatives.

Compound	DFDPP-C_2	DTDPP-C_2	DPDPP-C_2
(hetero)aromatic ring-DPP torsion (°)	1.95	2.37	31.25
C-C-N-C bond torsion (°)	95.77	91.79	80.05

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