Supporting Information

Generation of low-dimensional architectures through the self-assembly of pyromellitic diimide derivatives.

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1. Synthesis and analysis

**General information**

5,5’-(1,3,5,7-tetraoxopyrrolo[3,4-f]isoindole-2,6-diyl)diisophthalic acid 1 has been obtained by methodology reported previously. NMR spectra was run on a Varian VNMR-S 400 MHz spectrometer and was calibrated against the residual protonated solvent signals (CDCl\textsubscript{3} δ 7.24) and shifts are given in ppm. Electron impact mass spectra was obtained using a spectrometer Bruker 320MS/420GC. Microanalyses were obtained using a Perkin–Elmer 2400 CHN microanalyser.

**Synthesis of 5,5’-(1,3,5,7-tetraoxopyrrolo[3,4-f]isoindole-2,6-diyl)diisophthaloyl tetrachloride A:** A mixture of 5,5’-(1,3,5,7-tetraoxopyrrolo[3,4-f]isoindole-2,6-diyl)diisophthalic acid 1 (1.10 g; 2.0 mmol) and thionyl chloride (50 mL) were heated for 3 h at 90 °C under an argon atmosphere. Then the solvent was evaporated under reduced pressure to gave A as a white solid. Crude compound A was used immediately for the subsequent step of synthesis.

**Synthesis of methyl ester 2:** A suspension of 5,5’-(1,3,5,7-tetraoxopyrrolo[3,4-f]isoindole-2,6-diyl)diisophthaloyl tetrachloride A (1.25 g, 2.0 mmol) in methanol (30 mL) was heated at 80 °C for 48 h. Then the solvent was evaporated under reduced pressure, residue was dissolved in dichloromethane and white solid was precipitated by addition of hexane. The solid was filtered off and washed with small amount of hexane. Yield: 0.88 g (72 %). EI-MS m/z = 600.2 (90, M\textsuperscript{+}). \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}): δ = 8.72 (t, 2H, \textit{J} = 1.7 Hz), 8.52 (s, 2H), 8.37 (d, 4H, \textit{J} = 1.5 Hz), 3.98 (s, 12H) ppm. \textsuperscript{13}C-NMR (100 MHz, CDCl\textsubscript{3}): δ = 164.61, 164.29, 138.19, 133.46, 132.62, 132.45, 131.62, 120.58, 52.71 ppm. Elemental analysis calcd. for C\textsubscript{30}H\textsubscript{20}N\textsubscript{2}O\textsubscript{12} (600.49) C, 60.00; H, 3.36; N, 4.67. Found C, 59.83; H, 3.48; N, 4.59.
Synthesis of hexyl ester 3: A solution of 5,5’-(1,3,5,7-tetraoxopyrrolo[3,4-f]isoindole-2,6-diyl)diisophthaoyl tetrachloride A (1.32 g, 2.1 mmol) in hexanol (30 mL) was heated at 150 °C for 24 h under an argon atmosphere. Reaction mixture was concentrated to volume 10 mL under reduced pressure and cooled down in an ice bath. Obtained white solid was filtered off and washed with small amount of hexane. Yield: 1.28 g (68%). EI-MS m/z = 881.0 (100, M⁺). ¹H-NMR (400MHz, CDCl₃): δ = 8.76 (t, 2H, J = 1.7 Hz), 8.55 (s, 2H), 8.35 (d, 4H, J = 1.5 Hz), 4.38 (t, 8H, J = 6.8 Hz), 1.80 (q, 8H, J = 7.0 Hz), 1.35 (m, 24H, J = 4.1 Hz), 0.91 (t, 12H, J = 7.0 Hz) ppm. ¹³C-NMR (100 MHz, CDCl₃): δ = 164.68, 164.40, 137.01, 132.29, 131.28, 119.63, 65.95, 31.37, 28.53, 25.57, 22.48, 13.95 ppm. Elemental analysis calcd. for C₅₀H₆₀N₂O₁₂ (881.02) C, 68.16; H, 6.86; N, 3.18. Found C, 68.24; H, 6.95; N, 3.10.

Synthesis of hexyl amide 4: To a suspension of 5,5’-(1,3,5,7-tetraoxopyrrolo[3,4-f]isoindole-2,6-diyl)diisophthaoyl tetrachloride A (1.57 g, 2.5 mmol) in dry dichloromethane (40 mL) a solution of hexylamine (1.34 mL, 10.1 mmol) and triethylamine (1.41 mL, 10.1 mmol) was added at 0 °C. The yellow solution was mixed at room temperature for 24 h under an argon atmosphere and then was washed with water (50 mL), 1M HCl (50 mL) and brine (50 mL). Organic layer was dried over MgSO₄ and solvent was evaporated. Tetraamide 4 was obtained as a white solid by recrystallization form dichloromethane/isopropyl alcohol. Yield: 1.31 g (59 %). EI-MS m/z = 876.8 (80, M⁺). Elemental analysis calcd. for C₅₀H₆₄N₆O₈ (877.08) C, 68.47; H, 7.35; N, 9.58. Found C, 68.60; H, 7.42; N, 9.54.

Figure S2 ¹H-NMR spectra of 2 in CDCl₃.
Figure S3 $^{13}$C-NMR spectrum of 2 in CDCl$_3$. 
Figure S4 $^1$H-NMR spectrum of 3 in CDCl$_3$. 
Figure S5 $^{13}$C-NMR spectrum of 3 in CDCl$_3$. 
Figure S6 $^1$H-NMR of 4 in DMSO $d_6$
Figure S7 $^{13}$C-NMR spectrum of 4 in DMSO d$_6$.

Figure S8 $^1$H-NMR spectra of compound 4 in CDCl$_3$ and DMSO d$_6$. 
Figure S9 Variable temperature $^1$H-NMR spectra of 4 in CDCl$_3$
2. Atomic Force Microscopy

**Figure S10** Small assemblies of compound 1 from SIP. Particle distribution for the domains in Fig. 2a-inset of the main text. Aggregates on SiO$_2$ and mica with their corresponding section profiles.
Figure S11 Compound 1 after SVA treatment (Fig. 2e in main text). The section profile shows a layered structure with steps multiple of 1.3 nm.
Figure S12 Self-assembled structures of compound 2 from SIP (top, Fig. 2b in main text); and after SVA treatment (bottom, Fig. 2f in main text).
Figure S13 Self-assembled structures of compound 3 from SIP (top, Fig. 2c in main text); and after SVA treatment (bottom, Fig. 2g in main text).
Figure S14 Self-assembled structures of compound 4 from SIP (top, Fig. 2f in main text); and after SVA treatment (bottom, Fig. 2h in main text). The size of single fiber can be deduced from the section profiles.
3. IR spectroscopy

Infrared absorption spectra were studied within the mid-IR range (400 - 4000 cm\(^{-1}\)) by using Bruker Equinox 55 FT-IR spectrometer equipped with a KBr beam splitter. For temperature measurements the samples were placed on a KBr plate in THMS 600 Linkam heating stage equipped with a temperature controller. At the beginning the samples in the form of single crystal or powder were measured at room temperature. Subsequently, they were heated until melting to obtain thin films which were cooled down and heated again. Each temperature cycle was done between room temperature and temperature above melting point and the IR spectra were continuously collected. Before each measurement the sample temperature was stabilized for several minutes.

Figure S15 Schematic representation of two supramolecular motifs proposed for 1 as obtained upon varying the temperature.
Figure S16. Temperature dependence of IR spectra of solid 2 (a) and a thin film of 2 (b); in both cases the samples were heated until melting.

Figure S6. Temperature dependence of IR spectra of solid 3 (a) and a thin film of 3 (b); in both cases the samples were heated until melting.
Figure S7 Schematic representation of ordering upon heating/cooling cycle for compound 3.
4. UV-Vis spectra

Absorption spectra of compounds 2-4 were recorded with a Shimadzu UV-2401 PC spectrophotometer at concentrations $1 \times 10^{-5}$ M in dichloromethane at the room temperature. The absorption bands and molar absorption coefficients are listed in Table S1.

Table S1 Maximum absorption bands ($\lambda_{\text{max.}}$ [nm]) and molar absorption coefficients ($\varepsilon$ [$10^4$ $\text{dm}^3 \times \text{cm}^{-1} \times \text{mol}^{-1}$]) of the studied compounds.

| Compound | $\lambda_{\text{max.}}$ [nm] ($\varepsilon$ [$10^4$ $\text{M}^{-1} \text{cm}^{-1}$]) |
|----------|------------------------------------------------------------------|
| 2        | 234 (23.33), 251.5 (19.74), 321.5 (0.936)                         |
| 3        | 234.5 (20.86), 250 (16.27), 323 (0.94)                            |
| 4        | 233.5 (22.3), 248.5 (18.55), 325 (0.94)                           |

The electronic absorption spectra of compounds 2, 3 and 4 in the UV region showed typical bands for $\pi-\pi^*$ stacking ligand-based transitions at 230-350nm.

Figure S8 UV-Vis spectra of compounds 2 (─), 3 (─) and 4 (─) recorded in CH$_2$Cl$_2$ ($c = 1 \times 10^{-5}$ M).
5. Density Functional Theory (DFT)

All calculations were carried out using the Gaussian 09 application which is available through the PL-Grid portal [1]. Calculations were performed, within Density Functional Theory (DFT) [2] framework at M06/6-311G* level [3,4]. The M06 method was selected based on the results from extensive comparative studies, it is also recommended for calculations for organometallic and inorganometallic compounds and for non-covalent interactions [3]. Finally, to take into account the effect of solvent we used the Polarizable Continuum Model (PCM) [5] with dichloromethane and DMSO chosen as solvents as in the experimental studies. All figures depicting orbitals were prepared with use of Avogadro computer program [6].

Table S2 HOMO and LUMO energy levels and band gaps for compounds 1-4.

| compound | Vacuum | Dichloromethane | DMSO |
|----------|--------|------------------|------|
|          | HOMO [a.u.] | LUMO [a.u.] | Gap [eV] | HOMO [a.u.] | LUMO [a.u.] | Gap [eV] | HOMO [a.u.] | LUMO [a.u.] | Gap [eV] |
| 1        | -0.27119 | -0.15293 | -3.21802 | -0.27432 | -0.12304 | -4.11654 | -0.27417 | -0.12017 | -4.19056 |
| 2        | -0.28506 | -0.14159 | -3.90402 | -0.27895 | -0.12157 | -4.28253 | -0.27880 | -0.11994 | -4.32280 |
| 3        | -0.27699 | -0.14110 | -3.69776 | -0.28041 | -0.12102 | -4.33722 | -0.28032 | -0.11955 | -4.37478 |
| 4        | -0.28576 | -0.15099 | -3.66728 | -0.27246 | -0.12387 | -4.04334 | -0.27161 | -0.12191 | -4.07355 |

Figure S20. Representations of LUMO (top) and HOMO (middle) orbitals. The bottom row shows structural formulae of compounds 1-4.
6. Charge transport properties in field-effect transistors devices

In order to unravel the charge transport ability of all the above-mentioned materials, their electrical characterization was performed by integrating them in field-effect transistor (FET) devices whose active layer was composed of different self-assembled architectures of arylene di-imide derivative (1-4). Transistors in bottom-contact bottom-gate configuration were fabricated on n++ Si substrates with 230 nm of thermally grown SiO₂ as the gate dielectric and pre-patterned pairs of (bottom) gold electrodes with interdigitated geometry as the source and drain. The semiconductor layer was deposited by drop-casting from a solution in DMSO for compounds 3 and 4 or a chloroform/DMSO mixture (vol:vol ratio 9:1) for compounds 1 and 2. After drop-casting, films were dried at room temperature overnight. All samples were prepared and measured under N₂ atmosphere to avoid oxidative doping of the materials and ensure reproducibility of the experiments. Further, as these molecules are mainly an electron transporter as previously shown [7], the SiO₂ substrate was chemically functionalized with hexamethyldisilazane (HMDS) previously deposited by spin-coating and followed by annealing at 100° C for 1h. The HMDS treatment of the surface hinders trapping coming from hydroxyl groups, which are present on the SiO₂ surface in the form of silanols. [8]

Previous fluorinated arylene di-imide derivative showed mobilities in the order of 10⁻² cm²V⁻¹s⁻¹ which are several order of magnitude higher than what measured in compound 1, which feature mobilities in the 10⁻⁸⁻¹⁰⁻⁹ cm²V⁻¹s⁻¹ range. In addition, the injection barrier from the Au electrodes into the LUMO of all the compounds can also be associated with the low device mobility recorded. Conversely, the threshold voltage (V_{TH}) was found to be positive and close to +20 V. The sign of V_{TH} is consistent with the behaviour of an n-type field-effect transistor working in accumulation. Its absolute value could be, in first approximation, associated with a low number of structural/electronic defects i.e. traps.

![Figure S21. Electrical characterization of compound 1 (left) output characteristics recorded at different gate voltage values and (right) transfer characteristics recorded at V_{DS} = +120 V (W/L = 1000).](image)

The poor solubility and the consequent necessity of employing DMSO as a solvent could additionally account for these reduced performances, as solvent traces could be still present in
the film even after a temperature annealing. It is believed that high boiling point and dielectric constant solvents do not allow charge carriers to easily overcome the molecule-to-molecule energetic barrier represented by the solvation sphere. By and large, we believe that the use of DMSO as well as the difficult charge injection are the major responsible for the non-functioning devices when compounds 2, 3 and 4 are used as the active layer.

**FET Transistors** Bottom-contact-bottom-gate transistors were fabricated starting from SiO$_2$/Si-n$^{++}$ substrates. The thermally grown SiO$_2$ layer (230 nm) has a capacitance per unit area ($C_i$) of 15 nFcm$^{-2}$. Pre-patterned 40-nm-thick gold source and drain electrodes did not undergo any chemical functionalization. The FET substrates were cleaned with acetone (95% GC) and isopropyl alcohol (99.7% GC) in an ultrasonic bath (20 min/solvent) followed by a gentle drying under nitrogen gas. After that, the silicon oxide substrate was functionalized with hexamethyl disilazane (HMDS) by spin-coating 100 µL onto the substrate surface for 60 s at 1500 rpm, followed by thermal annealing at 100 °C for 1 h.
7. References
[1] “Introduction - Infrastruktura PL-Grid.” [Online]. Available: http://www.plgrid.pl/en/projects/plus/about_project. [Accessed: 13-Oct-2014].
[2] W. Kohn, A. D. Becke, and R. G. Parr, “Density Functional Theory of Electronic Structure,” J. Phys. Chem., vol. 100, no. 31, pp. 12974–12980, Jan. 1996.
[3] Y. Zhao and D. G. Truhlar, “The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals,” Theor. Chem. Acc., vol. 120, no. 1–3, pp. 215–241, May 2008.
[4] K. Raghavachari, J. S. Binkley, R. Seeger, and J. A. Pople, “Self-Consistent Molecular Orbital Methods. 20. Basis set for correlated wave-functions,” J. Chem. Phys., 72 (1980) 650-54.
[5] J. Tomasi, B. Mennucci, R. Cammi, Chem. Rev. 105 (2005) 2999.
[6] M. D. Hanwell, D. E. Curtis, D. C. Lonie, T. Vandermeersch, E. Zurek, and G. R. Hutchison, “Avogadro: an advanced semantic chemical editor, visualization, and analysis platform,” J. Cheminformatics, vol. 4, no. 1, p. 17, Aug. 2012.
[7] B. J. Jung, N. J. Tremblay, M. L. Yeh and H. E. Katz, Chem. Mat., 2011, 23, 568-582.
[8] L. L. Chua, J. Zaumseil, J. F. Chang, E. C. W. Ou, P. K. H. Ho, H. Sirringhaus and R. H. Friend, Nature, 2005, 434, 194-199.