

## Electronic Supplementary Information for:

# *Twist and Shout: A surprising synergy between aryl and N-substituents defines the computed charge transport properties in a series of crystalline diketopyrrolopyrroles*

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## SI.1 Materials synthesis, crystallography and theoretical modelling

### Materials and characterisation techniques

Unless otherwise specified, all starting materials and reagents were purchased from Fisher Scientific, Sigma-Aldrich or VWR and used as received without further purification. NMR spectra were determined using a Bruker AV3 400 MHz spectrometer (in CDCl<sub>3</sub>). Elemental analyses were carried out using the service provided at the University of Strathclyde in Glasgow, UK. FTIR analyses were carried out on the neat samples by attenuated total reflectance using a Thermo-Scientific Nicolet iS5 FTIR Spectrometer, with an iD5 ATR (Diamond) sampling accessory.

### Synthesis

#### **3,6-di(thiophene-2-yl)-pyrrolo[3,4-c]-pyrrole-1,4(2H,5H)-dione (TDPP)**

2-thiophenecarbonitrile (3.82 g, 35.3 mmol) was added to a solution of sodium t-amylate, prepared by dissolving sodium (1.8 g, 78.3 mmol) in anhydrous 2-methyl-2-butanol (120 mL), and the resulting mixture heated to reflux. Under vigorous stirring, dimethyl succinate (2.25 g, 25.5 mmol) dissolved in anhydrous 2-methyl-2-butanol (60 mL) was added over 3 h. After further stirring for 3 h at reflux temperature, the mixture was cooled to 60 °C and treated with methanol (60 mL) and hydrochloric acid (37 %, 20 mL). The precipitate was collected by filtration, washed with water, methanol and dichloromethane and then dried to give **TDPP** (1.90 g, 36.1 %) as an insoluble dark red/violet powder and used without further purification. IR (ATR)/cm<sup>-1</sup>: 3130 (NH), 3020 (ArH), 1666 (C=O), 1586 (C=C), 1544 (NH), 1495 (C=C), 1452 (C=C).

#### **3,6-di(furan-2-yl)-pyrrolo[3,4-c]-pyrrole-1,4(2H,5H)-dione (FDPP)**

As per the method described for **TDPP** using sodium (3.15 g, 0.14 mol) in 2-methyl-2-butanol (120 mL), 2-furoritrile (4.00 g, 43.4 mmol) and dimethyl succinate (3.14 g, 21.5 mmol) in 2-methyl-2-butanol (50 mL). The product **FDPP** (1.71 g, 29.6 %) was obtained as an insoluble dark red powder and used without further purification. IR (ATR)/cm<sup>-1</sup>: 3400 (NH, br), 3119 (ArH), 1673 (C=O), 1622 (C=C), 1556 (NH), 1476 (C=C), 1411 (C=C).

### **2,5-dibenzyl-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (TBDPP)**

A suspension of **TDPP** (1.90 g, 6.30 mmol) and anhydrous  $K_2CO_3$  (8.75 g, 63.30 mmol) in anhydrous DMF (90 mL) was heated at 120 °C under nitrogen atmosphere. At this temperature and under vigorous stirring a benzyl bromide (10.70 g, 62.60 mmol) solution in DMF (100 mL) was added over 1 h. Stirring and heating at 120 °C were continued for 2 h and after the addition of cold methanol/water (100 mL) the resulting precipitate was filtered and washed with methanol and then hexane. The crude product was recrystallised from dichloromethane:hexane (2:1) to give **TBDPP** (0.22 g, 7.00 %) as a dark red powder.  $^1H$  NMR (400 MHz, DMSO- $d_6$ ): 5.35 (4H, s,  $CH_2$ ), 7.22-7.38 (12H, m, ArH), 7.99 (2H, d, ArH), 8.67 (2H, d, ArH). IR (ATR)/ $cm^{-1}$ : 3100 (ArH), 2910 (CH), 1660 (C=O), 1555 (C=C), 1496 (C=C), 1439 (CH), 1395 (C=C). Anal. Calcd. for  $C_{28}H_{20}N_2O_2S_2$ : C, 69.97; H, 4.19; N, 5.83. Found: C, 69.49; H, 4.46; N, 5.65. Melting Point: 278-280 °C

### **2,5-dibenzyl-3,6-di(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (FBDPP)**

A suspension of **FDPP** (1.71 g, 6.38 mmol) and anhydrous  $K_2CO_3$  (8.00 g, 57.90 mmol) in anhydrous DMF (40 mL) was heated at 120 °C under nitrogen atmosphere. At this temperature and under vigorous stirring a benzyl bromide (9.52 g, 55.7 mmol) solution in DMF (50 mL) was added over 1.5 h. Stirring and heating at 120 °C were continued for 2 h and after the addition of cold methanol (100 mL) the resulting precipitate was filtered and washed with methanol. Purification of the crude product by wet flash column chromatography eluting with a gradient of dichloromethane in hexane gave **FBDPP** as a red powder (0.37 g, 13.0 %).  $^1H$  NMR (400 MHz, DMSO- $d_6$ ) 5.32 (4H, s,  $CH_2$ ), 6.87 (2H, dd, ArH), 7.21-7.33 (10H, m, ArH), 8.05 (2H, d, ArH), 8.12 (2H, d, ArH). IR (ATR)/ $cm^{-1}$ : 3010 (ArH), 2900 (CH), 1663 (C=O), 1584 (C=C), 1476 (C=C), 1442 (C=C), 1422 (CH). Anal. Calcd. for  $C_{28}H_{20}N_2O_4$ : C, 74.99; H, 4.50; N, 6.25. Found: C, 75.22; H, 4.78; N, 6.06. Melting Point: 270-272 °C

### **Preparation of crystals for single crystal X-ray diffraction analysis**

Single crystals of **TBDPP** and **FBDPP** were obtained from DCM/hexane (1:1) by slow evaporation of a cooled solution.

## Crystal structure determination

All measurements were made with an Oxford Diffraction Gemini S instrument. Refinement was to convergence against F2 and used all unique reflections. Hydrogen atoms were placed in idealized positions and refined in riding modes. Programs used were from the SHELX suite.<sup>1</sup> Selected crystallographic and refinement parameters are given in Table SI1.1. CCDC reference numbers 1506131 and 1506132 contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)

**Table SI1.1** Selected crystallographic data and refinement parameters for compounds **FBDPP** and **TBDPP**.

| Compound                                        | FBDPP                                                         | TBDPP                                                                        |
|-------------------------------------------------|---------------------------------------------------------------|------------------------------------------------------------------------------|
| Formula                                         | C <sub>28</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub> | C <sub>28</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub> S <sub>2</sub> |
| M <sub>r</sub> (g mol <sup>-1</sup> )           | 448.46                                                        | 480.58                                                                       |
| Crystal system                                  | monoclinic                                                    | monoclinic                                                                   |
| Space group                                     | C2/c                                                          | P2 <sub>1</sub> /n                                                           |
| Temperature (K)                                 | 123(2)                                                        | 123(2)                                                                       |
| <i>a</i> (Å)                                    | 23.385(2)                                                     | 5.5724(3)                                                                    |
| <i>b</i> (Å)                                    | 5.3635(4)                                                     | 11.3414(7)                                                                   |
| <i>c</i> (Å)                                    | 17.4866(16)                                                   | 17.3547(9)                                                                   |
| β (°)                                           | 110.455(10)                                                   | 96.822(5)                                                                    |
| <i>V</i> /Å <sup>3</sup>                        | 2055.0(3)                                                     | 1089.03(11)                                                                  |
| <i>Z</i>                                        | 4                                                             | 2                                                                            |
| Wavelength (Å)                                  | 1.5418                                                        | 1.5418                                                                       |
| Measured reflections                            | 3952                                                          | 4332                                                                         |
| Unique reflections                              | 1947                                                          | 2123                                                                         |
| <i>R</i> <sub>int</sub>                         | 0.0419                                                        | 0.0373                                                                       |
| Observed rflns [ <i>I</i> > 2σ( <i>I</i> )]     | 1246                                                          | 1727                                                                         |
| μ (mm <sup>-1</sup> )                           | 0.797                                                         | 2.465                                                                        |
| No. of parameters                               | 154                                                           | 226                                                                          |
| 2θ <sub>max</sub> (°)                           | 139.8                                                         | 146.42                                                                       |
| <i>R</i> [on <i>F</i> , obs rflns only]         | 0.0508                                                        | 0.0569                                                                       |
| <i>wR</i> [on <i>F</i> <sup>2</sup> , all data] | 0.1346                                                        | 0.1642                                                                       |
| GoF                                             | 1.040                                                         | 1.077                                                                        |
| Largest diff. peak/hole/e Å <sup>-3</sup>       | 0.183/−0.263                                                  | 0.437/−0.335                                                                 |

## Computational details

Unless otherwise stated, all quantum mechanical calculations reported herein were carried out using Truhlar's density functional M06-2X<sup>2</sup> at 6-311G(d) level as implemented in Spartan '10 software.<sup>3</sup> All nearest neighbour dimer pairs were extracted from experimentally determined single crystal structures using a cut-off distance of van-der-Waals (vdW) radius + 0.3 Å. Intermolecular interaction energies were corrected for Basis Set Superposition Error (BSSE) using the counterpoise method of Boys and Bernardi.<sup>4</sup> Hole ( $t_h$ ) and electron ( $t_e$ ) transfer integrals were computed for centrosymmetric dimer pairs within the framework of the energy splitting in dimer method,<sup>5</sup> where  $t_h$  and  $t_e$  are given by half the splitting between the HOMO/HOMO(-1) and LUMO/LUMO(+1) supramolecular orbitals respectively. Computed model systems for **TDPP** and **FDPP** were generated following the method described by us previously.<sup>6</sup> Geometries of **TDPP** and **FDPP** were optimised using M06-2X<sup>2</sup>/6-311G(d) while keeping DPP-thiophene/furan dihedral angles constrained to 0°. The two monomers of **TDPP**/**FDPP** were mutually aligned in a fully eclipsed manner at an intermonomer distance,  $\Delta z = 3.6$  Å and one monomer was displaced with respect to the other along the long molecular axis in 0.3 Å increments for 15.3 Å while keeping  $\Delta y = 0.0$  and  $\Delta z = 3.6$  Å. Inner sphere reorganisation energies were estimated using DPP core – phenyl/thiophene/furan rings dihedral angle extracted from experimentally determined single crystal structures and model systems generated following the method previously described by us,<sup>7</sup> where these are computed by constraining the DPP core-phenyl/thiophene/furan ring dihedral angle from  $\theta = 0$  to 90° in 10° increments. The total hole/electron inner-sphere reorganisation energy can be broken down into two different contributions: i) reorganisation energy associated to the progression from neutral to radical cation/anion,  $\lambda^{NR}$  ( $\lambda^{NR} = E_{Rgeom}^N - E_{Ngeom}^N$ ) and ii) on going from radical cation/anion to neutral geometry,  $\lambda^{RN}$  ( $\lambda^{RN} = E_{Ngeom}^R - E_{Rgeom}^R$ ), where  $E_{Ngeom}^N$  is the energy of the neutral species at its equilibrium geometry and  $E_{Rgeom}^N$  denotes the energy of the neutral species at the equilibrium geometry of the radical species. Analogously,  $E_{Rgeom}^R$  represents the energy of the radical species at its equilibrium geometry and  $E_{Ngeom}^R$  is the energy of the radical species at the equilibrium geometry of the neutral.<sup>5, 8-10</sup> To further validate these model systems, inner-sphere reorganisation energies were computed for fully optimised geometries of non N-substituted systems (**PDPP**, **TDPP** and **FDPP**) and N-methyl substituted architectures (**PMDPP**, **TMDPP** and **FMDPP**). Neutral and radical cation/anion energies and

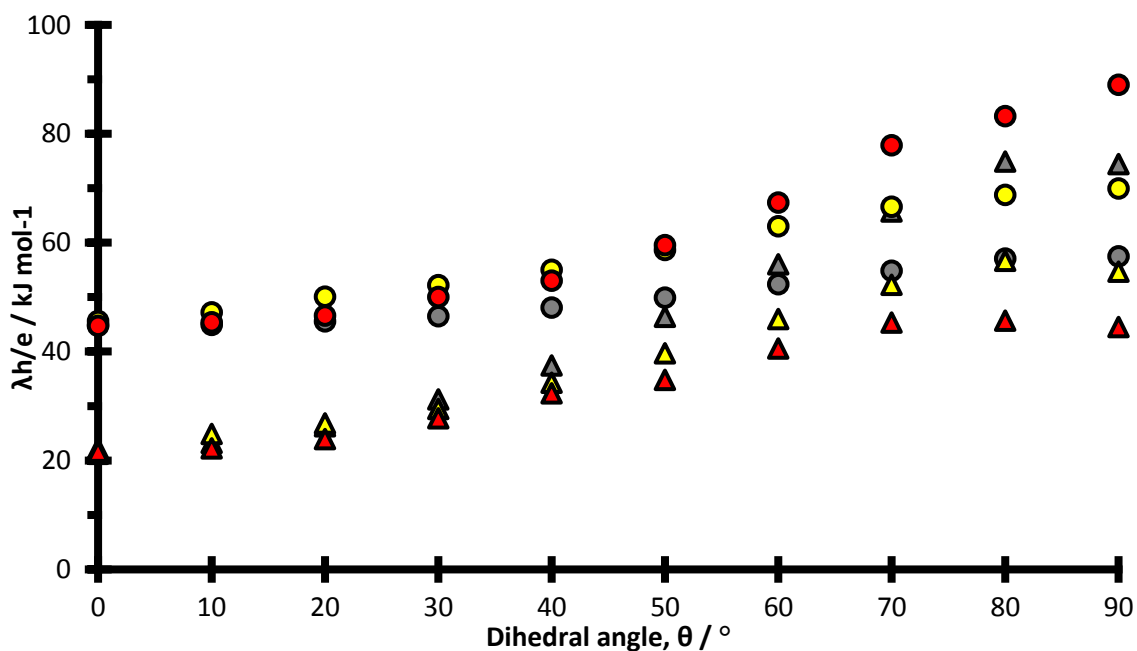
geometries were determined using restricted and unrestricted DFT methods respectively. For all radical ion species  $0.75 < S^2 < 0.78$ , which indicates acceptably low spin-contamination in all cases. All unconstrained equilibrium geometries were confirmed by calculated IR, with all spectra confirming the true equilibrium minima by the absence of imaginary modes.<sup>11-13</sup>

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## SI.2 Computed inner-sphere reorganisation energies for fully optimised geometries of FDPP, PDPP, TDPP, FMDPP, PMDPP and TMDPP and associated model systems

**Table SI.2.1** Computed inner-sphere reorganisation energies for hole ( $\lambda_h$ ) and electron ( $\lambda_e$ ) for fully optimised geometries of **FDPP**, **PDPP**, **TDPP**, **FMDPP**, **PMDPP** and **TMDPP**. M06-2X/6-311G(d)

| System       | $\lambda_h / \text{kJ mol}^{-1}$ | $\lambda_e / \text{kJ mol}^{-1}$ |
|--------------|----------------------------------|----------------------------------|
| <b>FDPP</b>  | 44.77                            | 21.46                            |
| <b>PDPP</b>  | 47.56                            | 25.89                            |
| <b>TDPP</b>  | 47.00                            | 22.50                            |
| <b>FMDPP</b> | 44.61                            | 21.08                            |
| <b>PMDPP</b> | 51.10                            | 34.03                            |
| <b>TMDPP</b> | 47.42                            | 21.82                            |



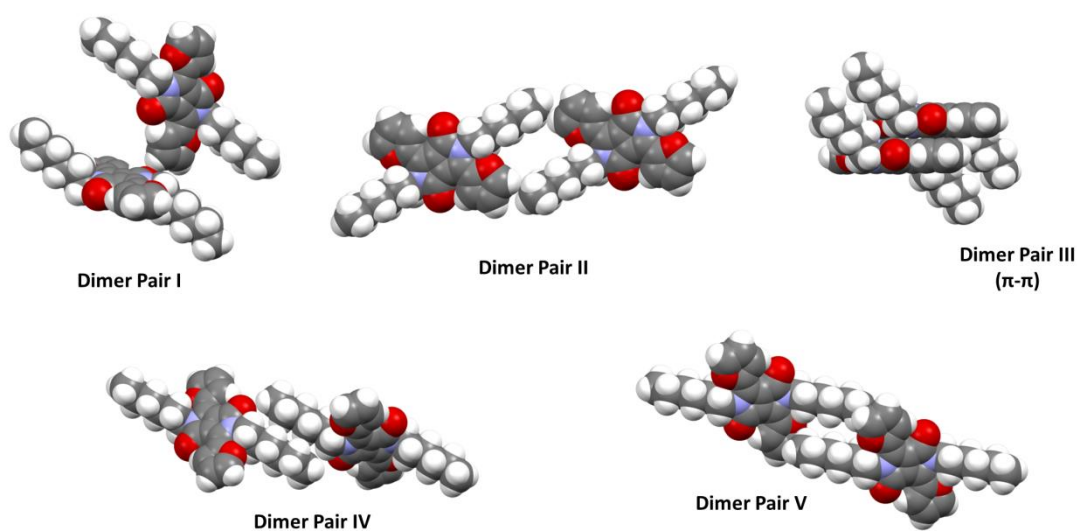
**Figure SI.2.1** Computed inner-sphere reorganisation energies towards hole,  $\lambda_h$  (filled circles) and electron,  $\lambda_e$  (filled triangles) transfer for **PDPP** (grey), **TDPP** (yellow) and **FDPP** (red).

### SI.3 Nearest neighbour dimer pairs and interaction energies of *XYDPPs*

**Table SI.3.1** Number of equivalent molecules, site and computed intermolecular interaction for non-structurally modified and cropped dimer pairs of *FADPP*

| Dimer pair            | No eq. molecules | Site <sup>a</sup> | $\Delta E_{CP} / \text{kJ mol}^{-1}$ |        |        |        |
|-----------------------|------------------|-------------------|--------------------------------------|--------|--------|--------|
|                       |                  |                   | XYDPP                                | XDPP   | YDPP   | DPP    |
| I                     | 4                | (1/2,1,0)         | -9.31                                | -9.29  | 0.17   | -0.84  |
| II                    | 2                | (1,3/2,1/2)       | -3.52                                | -0.25  | -0.02  | 0.42   |
| III ( $\pi$ - $\pi$ ) | 2                | (1/2,1,1/2)       | -72.00                               | -56.58 | -24.72 | -12.91 |
| IV                    | 4                | (0,-1/2,0)        | -10.53                               | -0.20  | -10.39 | -0.04  |
| V                     | 2                | (1,1/2,1/2)       | -9.94                                | -0.58  | -2.62  | 0.09   |

<sup>a</sup> Around the monomer at (1/2,0,1/2)



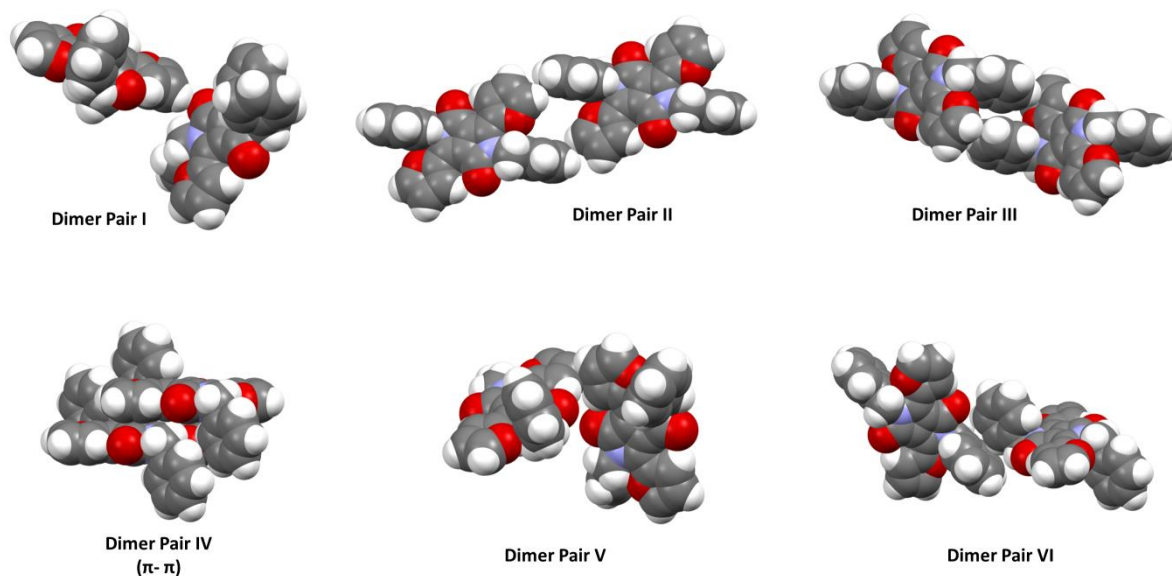
**Figure SI.3.1** Spaced-filled illustration of the different nearest neighbour dimers of *FADPP*.



**Table SI.3.2** Number of equivalent molecules, site and computed intermolecular interaction for non-structurally modified and cropped dimer pairs of **FBDPP**

| Dimer pair           | No eq. molecules | Site <sup>a</sup> | $\Delta E_{CP} / \text{kJ mol}^{-1}$ |        |        |        |
|----------------------|------------------|-------------------|--------------------------------------|--------|--------|--------|
|                      |                  |                   | XYDPP                                | XDPP   | YDPP   | DPP    |
| I                    | 4                | (0,1,1/2)         | -9.79                                | -9.31  | -0.63  | -0.82  |
| II                   | 2                | (1/2,3/2,0)       | -5.78                                | 0.03   | 0.03   | 0.16   |
| III                  | 2                | (1/2,1/2,0)       | -15.61                               | -0.34  | -4.20  | -0.01  |
| IV ( $\pi$ - $\pi$ ) | 2                | (0,1,0)           | -78.53                               | -45.11 | -34.25 | -12.01 |
| V                    | 2                | (0,0,1/2)         | -0.14                                | -1.08  | 1.99   | 1.35   |
| VI                   | 2                | (1/2,-1/2,1/2)    | -13.93                               | -0.13  | -16.24 | -0.10  |

<sup>a</sup> Around the monomer at (0,0,0)

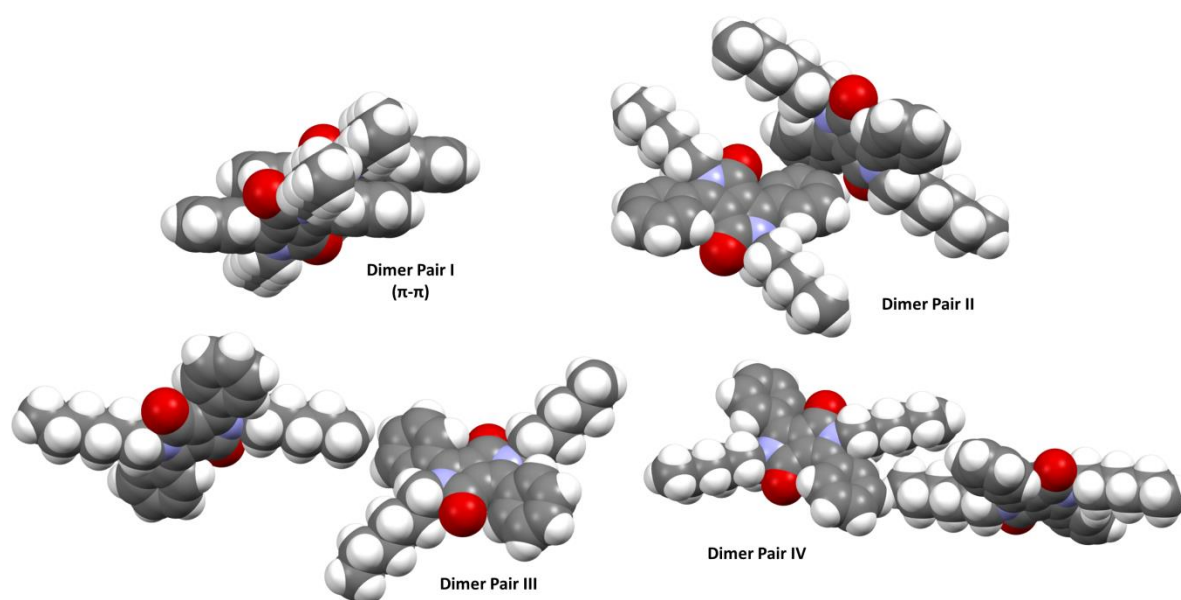


**Figure SI.3.2** Spaced-filled illustration of the different nearest neighbour dimers of **FBDPP**.

**Table SI.3.3** Number of equivalent molecules, site and computed intermolecular interaction for non-structurally modified and cropped dimer pairs of *PADPP*

| Dimer pair          | No eq. molecules | Site <sup>a</sup> | $\Delta E_{CP} / \text{kJ mol}^{-1}$ |        |        |       |
|---------------------|------------------|-------------------|--------------------------------------|--------|--------|-------|
|                     |                  |                   | XYDPP                                | XDPP   | YDPP   | DPP   |
| I ( $\pi$ - $\pi$ ) | 2                | (0,-1,0)          | -59.94                               | -33.21 | -10.90 | -3.77 |
| II                  | 4                | (0,-1/2,-1/2)     | -18.52                               | -19.05 | -1.41  | -1.62 |
| III                 | 4                | (-1,3/2,-1/2)     | -0.75                                | 0.32   | -0.43  | 0.13  |
| IV                  | 4                | (-1,-1/2,-1/2)    | -3.79                                | 0.01   | -3.09  | 0.46  |

<sup>a</sup> Around the monomer at (0,0,0)

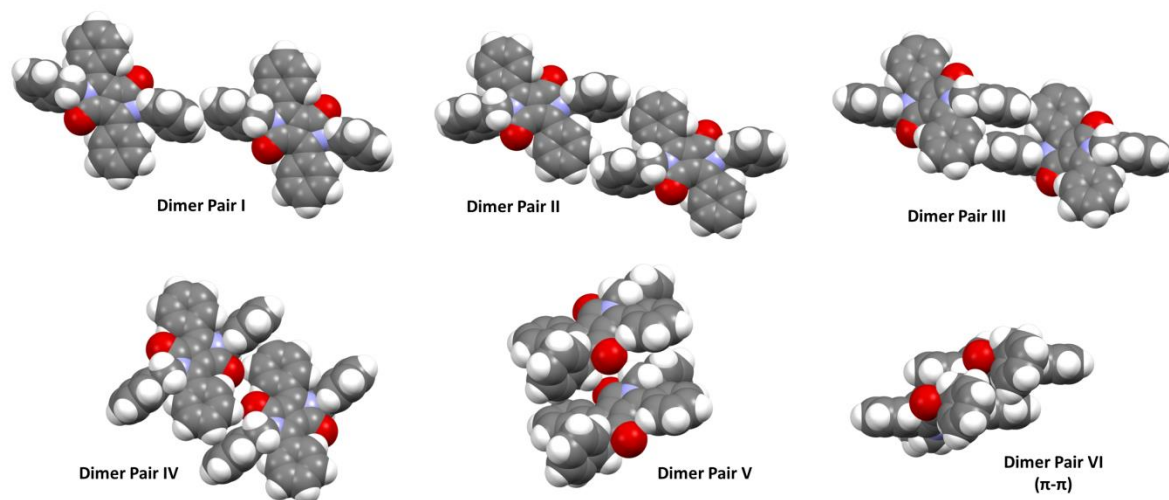


**Figure SI.3.3** Spaced-filled illustration of the different nearest neighbour dimers of *PADPP*.

**Table SI.3.4** Number of equivalent molecules, site and computed intermolecular interaction for non-structurally modified and cropped dimer pairs of **PBDPP**

| Dimer pair           | No eq. molecules | Site <sup>a</sup> | $\Delta E_{CP} / \text{kJ mol}^{-1}$ |        |        |        |
|----------------------|------------------|-------------------|--------------------------------------|--------|--------|--------|
|                      |                  |                   | XYDPP                                | XDPP   | YDPP   | DPP    |
| I                    | 2                | (0,1,1)           | -6.05                                | -0.39  | -5.78  | -0.28  |
| II                   | 2                | (1,0,1)           | -4.46                                | 0.88   | 0.11   | 0.26   |
| III                  | 2                | (0,0,1)           | -11.21                               | -0.45  | -5.20  | -0.06  |
| IV                   | 2                | (-1,1,0)          | -31.36                               | -8.78  | 1.93   | 3.99   |
| V                    | 2                | (0,1,0)           | -24.15                               | -3.42  | -15.48 | -4.88  |
| VI ( $\pi$ - $\pi$ ) | 2                | (1,0,0)           | -70.12                               | -41.89 | -28.58 | -12.12 |

<sup>a</sup> Around the monomer at (0,0,0)

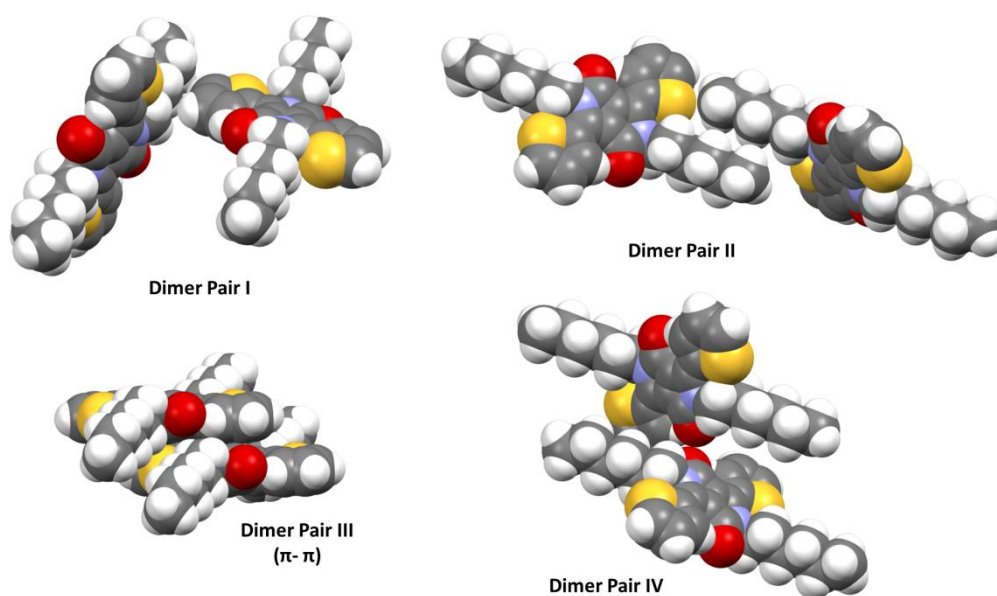


**Figure SI.3.4** Spaced-filled illustration of the different nearest neighbour dimers of **PBDPP**.

**Table SI.3.5** Number of equivalent molecules, site and computed intermolecular interaction for non-structurally modified and cropped dimer pairs of **TADPP**

| Dimer pair            | No eq. molecules | Site <sup>a</sup> | $\Delta E_{CP} / \text{kJ mol}^{-1}$ |        |        |        |
|-----------------------|------------------|-------------------|--------------------------------------|--------|--------|--------|
|                       |                  |                   | XYDPP                                | XDPP   | YDPP   | DPP    |
| I                     | 4                | (1/2,-<br>1,1/2)  | -3.77                                | 1.48   | -0.07  | -0.28  |
| II                    | 4                | (3/2,1,4/3)       | -6.70                                | 0.37   | -5.14  | 0.20   |
| III ( $\pi$ - $\pi$ ) | 2                | (1/2,-<br>1/2,1)  | -65.45                               | -51.13 | -18.95 | -12.66 |
| IV                    | 2                | (1/2,0,3/2)       | -19.81                               | -8.30  | 1.14   | 1.76   |

<sup>a</sup> Around the monomer at (1/2,1/2,1))

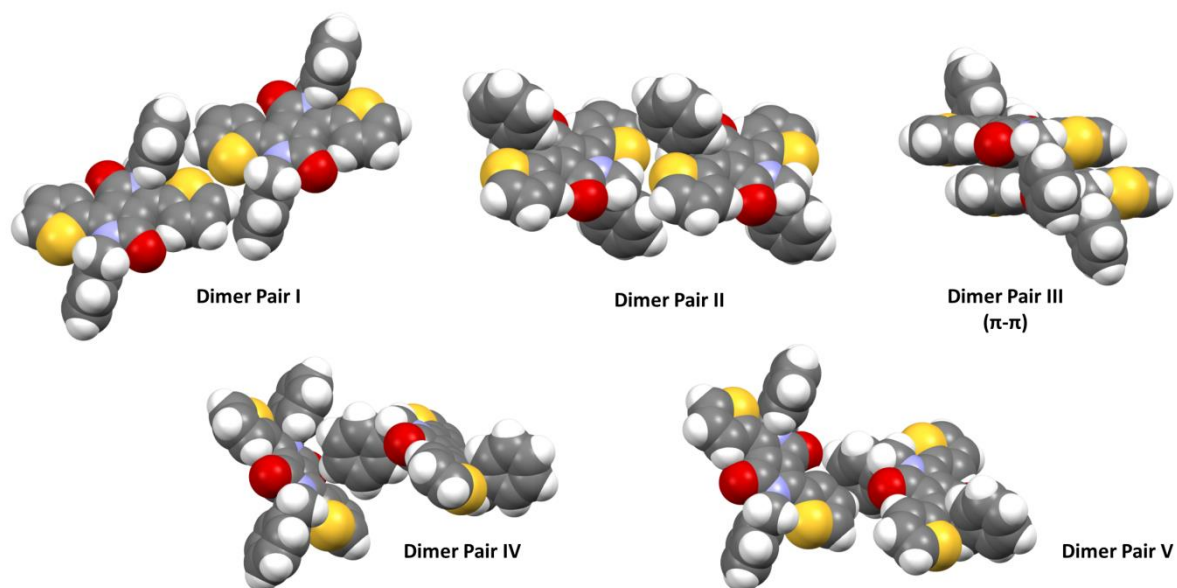


**Figure SI.3.5** Spaced-filled illustration of the different nearest neighbour dimers of **TADPP**.

**Table SI.3.6** Number of equivalent molecules, site and computed intermolecular interaction for non-structurally modified and cropped dimer pairs of **TBDPP**

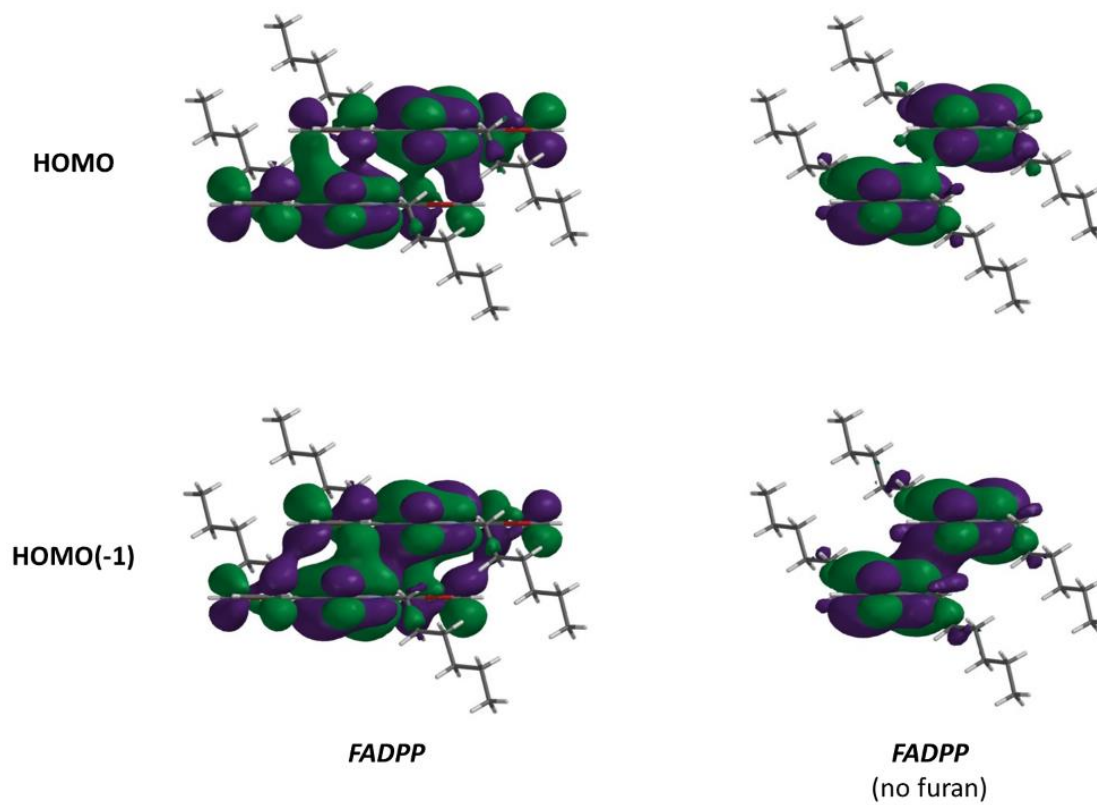
| Dimer pair            | No eq. molecules | Site <sup>a</sup> | $\Delta E_{CP} / \text{kJ mol}^{-1}$ |        |        |       |
|-----------------------|------------------|-------------------|--------------------------------------|--------|--------|-------|
|                       |                  |                   | XYDPP                                | XDPP   | YDPP   | DPP   |
| I                     | 2                | (-1,1,0)          | -26.68                               | -2.95  | -1.70  | 0.55  |
| II                    | 2                | (0,1,0)           | -4.73                                | -1.25  | 0.87   | 1.82  |
| III ( $\pi$ - $\pi$ ) | 2                | (1,0,0)           | -74.47                               | -27.26 | -35.48 | -2.18 |
| IV                    | 2                | (-1/2,1/2,-1/2)   | -10.75                               | -0.24  | -6.74  | -0.27 |
| V                     | 2                | (-1/2,1/2,1/2)    | -13.17                               | -0.55  | -5.11  | -1.48 |

<sup>a</sup> Around the monomer at (0,0,0)

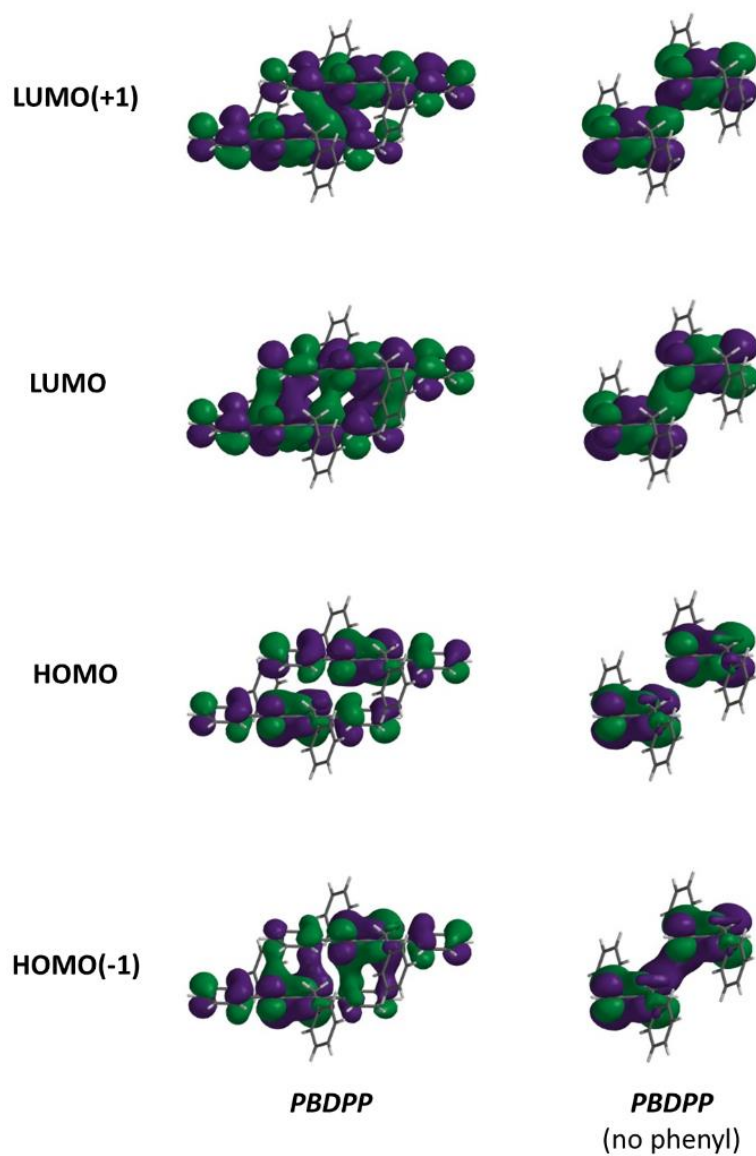


**Figure SI.3.6** Spaced-filled illustration of the different nearest neighbour dimers of **TBDPP**.

## SI.4 Supramolecular orbitals of FADPP and PBDPP



**Figure SI.4.1** Illustration of the HOMO and HOMO(-1) supramolecular orbitals of non-structurally modified and structurally modified (no furan) *FADPP*



**Figure SI.4.2** Illustration of the supramolecular orbitals of non-structurally modified and structurally modified (no phenyl) **PBDPP**