*Electronic Supporting Information*

# Non-Innocent Base Properties of 3- and 4-Pyridyl-Dithia- and Diselenadiazolyl Radicals; the Effect of *N*-Methylation.

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**Table S1.** Single crystal data for neutral dimers.

| Compound | 3-pyDTDA | 3-pyDSDA | 4-pyDSDA |
|---|---|---|---|
| CCDC Code [a] | 1863391 [b] | 1863392 | 1863394 |
| Formula | $C_6H_4N_3S_2$ | $C_6H_4N_3Se_2$ | $C_6H_4N_3Se_2$ |
| *fw*, g mol$^{-1}$ | 182.24 | 276.04 | 276.04 |
| *a*, Å | 6.3132(4) | 6.1517(1) | 16.385(1) |
| *b*, Å | 15.8613(9) | 16.5228(2) | 9.4978(6) |
| *c*, Å | 7.1082(4) | 7.3013(1) | 10.7059(8) |
| $\alpha$, deg | 90 | 90 | 90 |
| $\beta$, deg | 95.801(3) | 95.4320(10) | 120.387(4) |
| $\gamma$, deg | 90 | 90 | 90 |
| *V*, Å$^3$ | 708.14(6) | 738.796(18) | 1437.23(18) |
| $\rho$(calcd), g cm$^{-1}$ | 1.709 | 2.482 | 2.551 |
| space group | $P2_1$ | $P2_1$ | $C2/c$ |
| *Z* | 4 | 4 | 8 |
| Temp, K | 296(2) | 296(2) | 296(2) |
| $\mu$, mm$^{-1}$ | 0.622 | 9.935 | 10.214 |
| $\lambda$, Å | 0.68890 | 0.71073 | 0.71073 |
| data/restraints/params | 2773, 1, 200 | 4266, 1, 199 | 2078, 0, 100 |
| solution method | direct methods | direct methods | direct methods |
| $R, R_w$ (on $F^2$) | 0.0329, 0.0690 | 0.0193, 0.0349 | 0.0268, 0.0618 |

[a] Crystallographic data in CIF format can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing to data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, 889 Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

[b] These parameters may be compared with those obtained from a data set collected at 160 K and deposited in the Cambridge Crystallographic Database. See Clegg, W.; Elsegood, M. R. J. CCDC 1500537: *Experimental Crystal Structure Determination*, **2016**, DOI: 10.5517/ccdc.csd.cc1mcffv.

**Table S2.** Powder diffraction crystal data[a] for 4-pyDTDA.

| 4-pyDTDA Dimer | *cis*-cofacial[b] | *trans*-cofacial[c] | *trans*-antarafacial[c] |
|---|---|---|---|
| Formula | $C_6H_4N_3S_2$ | $C_6H_4N_3S_2$ | $C_6H_4N_3S_2$ |
| *fw*, g mol$^{-1}$ | 182.24 | 182.24 | 182.24 |
| *a*, Å | 15.4599(9) | 15.4604(10) | 15.4378(9) |
| *b*, Å | 8.9795(14) | 9.1679(23) | 9.0441(17) |
| *c*, Å | 11.3759(4) | 11.3749(4) | 11.3877(4) |
| $\alpha$, deg | 90 | 90 | 90 |
| $\beta$, deg | 119.888(3) | 119.950(4) | 119.826 |
| $\gamma$, deg | 90 | 90 | 90 |
| *V*, Å$^3$ | 1369.2(2) | 1397.0(4) | 1379.4(3) |
| $\rho$(calcd), g cm$^{-1}$ | 1.768 | 1.733 | 1.755 |
| space group | *C*2/*c* | *C*2/*c* | *C*2/*c* |
| *Z* | 8 | 8 | 8 |
| Temp, K | 293(2) | 293(2) | 293(2) |
| $\lambda$, Å | 0.825925 | 0.825925 | 0.825925 |
| solution method | powder data | powder data | powder data |
| $R_w, R_{wp}$ | 0.0680, 0.0950 | 0.0757, 0.1053 | 0.0713, 0.1006 |

[a] The three sets of cell parameters originate from Rietveld refinements of three different simulated annealing solutions obtained from the *same* experimental data.

[b] Crystallographic data in CIF format (CCDC 1863393) for this model are available free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing to data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, 889 Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

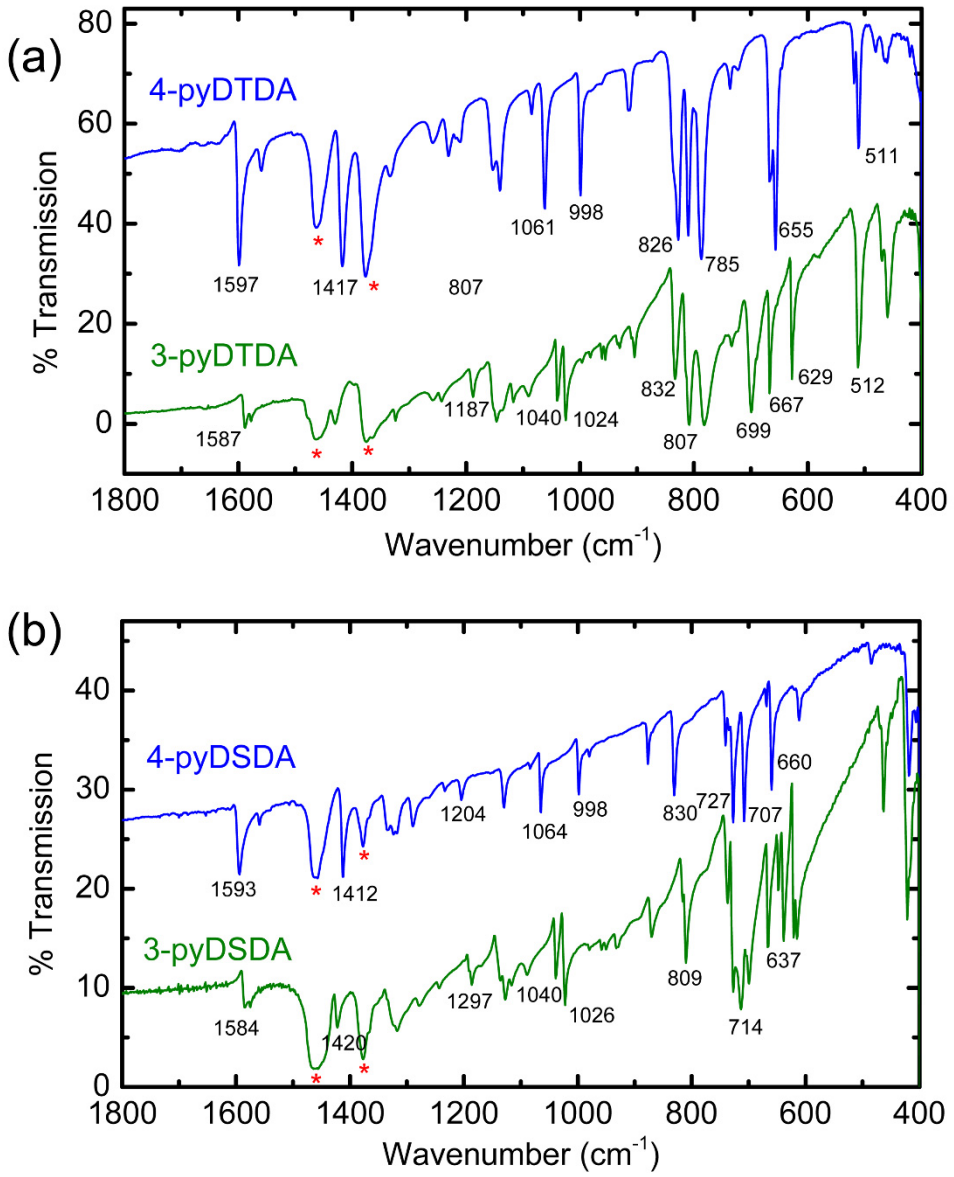
[c] Rietveld refined crystal coordinates for this model are listed in Tables S4/S5.

**Table S3.** Single crystal data for *N*-methylated dimers.

| Compound | Me[3-pyDTDA][OTf]$_2$ | Me[3-pyDTDA][OTf] | Me[4-pyDTDA][OTf]$_2$ | Me[4-pyDTDA][OTf] |
|---|---|---|---|---|
| CCDC Code [a] | 1863395 | 1863396 | 1863397 | 1863398 |
| Formula | $C_9H_7N_3O_6F_6S_4$ | $C_7H_7N_3O_3F_3S_4$ | $C_9H_7N_3O_6F_6S_4$ | $C_7H_7N_3O_3F_3S_4$ |
| *fw*, g mol$^{-1}$ | 495.42 | 346.35 | 495.42 | 346.35 |
| *a*, Å | 8.1075(6) | 6.1736(3) | 8.0170(4) | 13.9891(5) |
| *b*, Å | 10.6217(8) | 7.3729(3) | 9.9759(8) | 7.5092(2) |
| *c*, Å | 11.5431(7) | 14.0583(7) | 11.5580(10) | 12.1919(4) |
| $\alpha$, deg | 110.589(6) | 75.959(4) | 86.225(2) | 90 |
| $\beta$, deg | 91.928(6) | 89.336(4) | 76.718(2) | 101.367(3) |
| $\gamma$, deg | 108.236(7) | 86.857(4) | 72.963(3) | 90 |
| *V*, Å$^3$ | 872.21(12) | 619.84(5) | 860.16(11) | 1255.60(7) |
| $\rho$(calcd), g cm$^{-1}$ | 1.886 | 1.856 | 1.913 | 1.832 |
| space group | *P*1 | $P\bar{1}$ | $P\bar{1}$ | $P2_1/c$ |
| *Z* | 2 | 2 | 2 | 4 |
| Temp, K | 120.0(1) | 120.0(1) | 120.0(1) | 120.0(1) |
| $\mu$, mm$^{-1}$ | 5.98 | 5.99 | 0.651 | 5.912 |
| $\lambda$, Å | 1.54184 | 1.54184 | 0.71073 | 1.54184 |
| data/restraints/ params | 3128, 0, 254 | 2232, 0, 182 | 3144, 0, 254 | 2212, 0, 182 |
| solution method | direct methods | direct methods | direct methods | direct methods |
| $R$, $R_w$ (on $F^2$) | 0.0359, 0.0882 | 0.0291, 0.0720 | 0.0235, 0.0591 | 0.0351, 0.0846 |

[a] Crystallographic data in CIF format can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing to data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, 889 Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

**Figure S1.** FTIR spectra[a] of (a) 3, 4-pyDTDA and (b) 3, 4-pyDSDA.




[a] Spectra recorded on samples prepared in nujol mulls; bands associated with nujol are indicated by a red asterisk. Selected frequencies are indicated (in wavenumbers).

**Figure S2.** Observed and calculated PXRD pattern for *trans*-cofacial 4-pyDTDA.

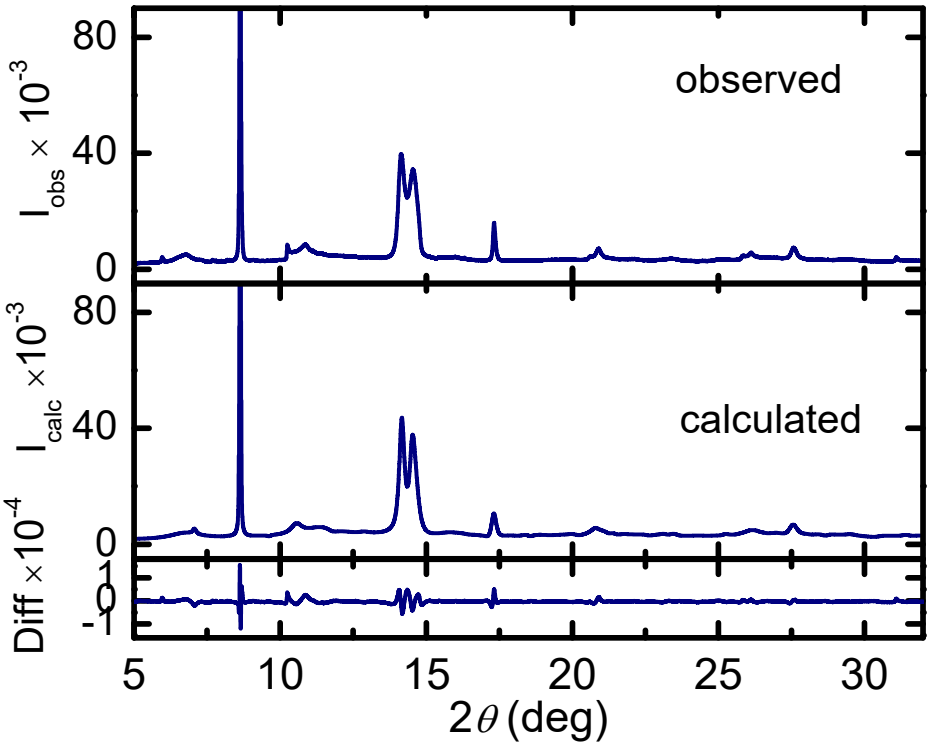



**Figure S3.** Observed and calculated PXRD pattern for *trans*-antarafacial 4-pyDTDA.

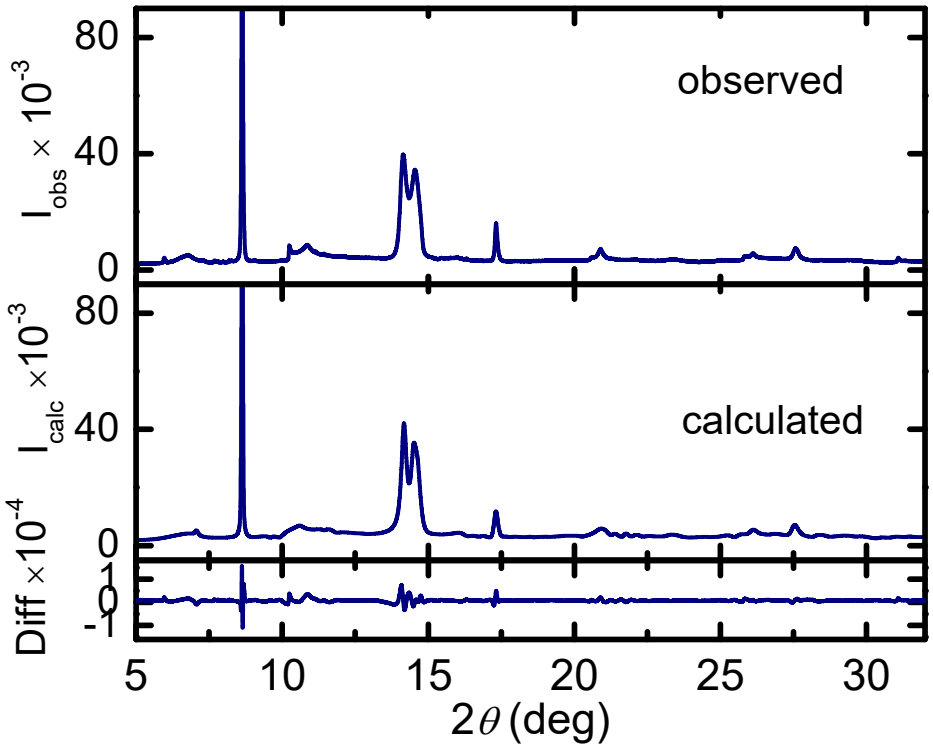
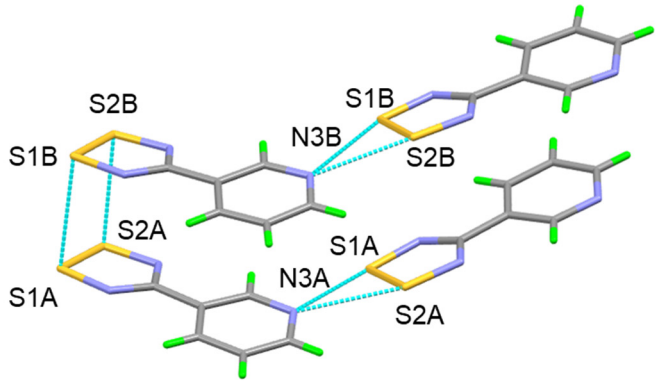


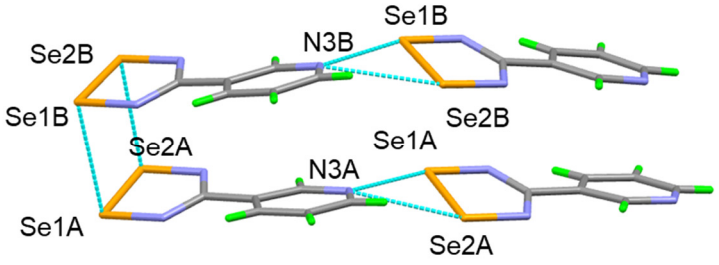
**Figure S4.** Intermolecular contacts (in Å) in (a) 3-pyDTDA and (b) 3-pyDSDA.

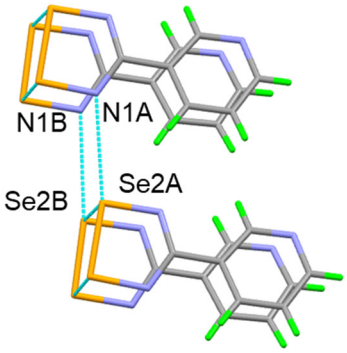
**3-pyDTDA**




| | |
|---|---|
| S1B···S1A | 3.188(2) |
| S2B···S2A | 3.144(2) |
| N3B···S1B | 2.963(4) |
| N3B···S2B | 2.868(3) |
| N3A···S1A | 2.846(4) |
| N3A···S2A | 2.970(3) |

**3-pyDSDA**



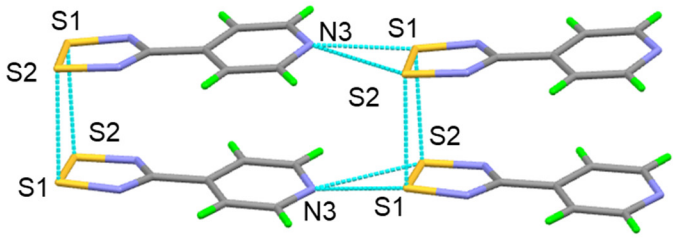

| | |
|---|---|
| Se1B···Se1A | 3.3094(5) |
| Se2B···Se2A | 3.2404(5) |

| | |
|---|---|
| N3B···Se1B | 2.906(3) |
| N3B···Se2B | 3.174(3) |
| N3A···Se1A | 3.074(3) |
| N3A···Se2A | 3.065(3) |

| | |
|---|---|
| N1A···Se2A | 3.411(3) |
| N1B···Se2B | 3.406(3) |

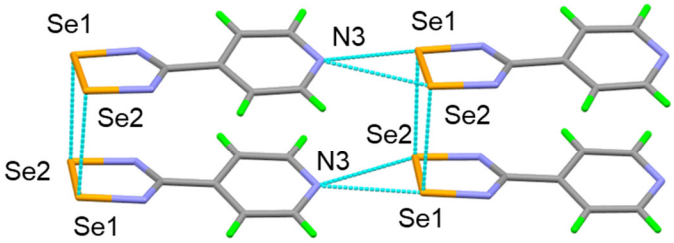
**Figure S5.** Intermolecular contacts (in Å) in (a) *cis*-cofacial 4-pyDTDA[a] and (b) 4-pyDSDA.

**4-pyDTDA**

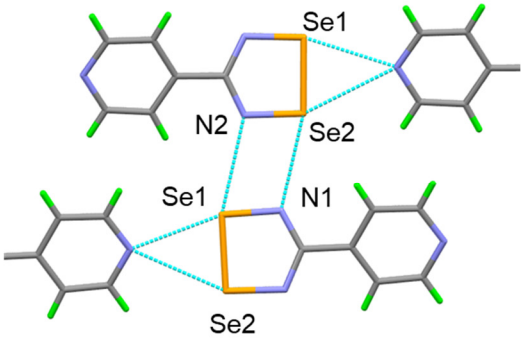



| | |
|---|---|
| S1···S2 | 3.100 |
| S1···N3 | 2.717 |
| S2···N3 | 2.952 |

**4-pyDSDA**




| | |
|---|---|
| Se1···Se2 | 3.2527(4) |
| Se1···N3 | 2.962(3) |
| N3···Se2 | 3.172(3) |




| | |
|---|---|
| Se1···N2 | 3.212(3) |
| Se2···N1 | 3.169(3) |

[a] Standard deviations on distances are not available for 4-pyDTDA.

**Table S4.** Crystal coordinates for *trans*-cofacial 4-pyDTDA (from Rietveld refinement).

```
data_trans-cofacial
_symmetry_cell_setting              monoclinic
_symmetry_space_group_name_H-M      'C 2/c'
_symmetry_Int_Tables_number         15
_space_group_name_Hall              '-C 2yn'
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1 x,y,z
2 -x,y,1/2-z
3 -x,-y,-z
4 x,-y,1/2+z
5 1/2+x,1/2+y,z
6 1/2-x,1/2+y,1/2-z
7 1/2-x,1/2-y,-z
8 1/2+x,1/2-y,1/2+z
_cell_length_a                      15.4604(10)
_cell_length_b                      9.1679(23)
_cell_length_c                      11.3749(4)
_cell_angle_alpha                   90.0
_cell_angle_beta                    119.950(4)
_cell_angle_gamma                   90.0
_cell_volume                        1396.97
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
S1 S 0.61891 0.37949 -0.54562
S2 S 0.66698 0.36935 -0.68694
N1 N 0.60491 0.20281 -0.5419
N2 N 0.66059 0.19151 -0.69928
C1 C 0.62987 0.12784 -0.62095
C2 C 0.62296 -0.03305 -0.62145
C3 C 0.65946 -0.1167 -0.68999
C6 C 0.6516 -0.26634 -0.69213
C5 C 0.57158 -0.2505 -0.55837
C6 C 0.58034 -0.10186 -0.55463
H3 H 0.68922 -0.07005 -0.73454
H4 H 0.67723 -0.32341 -0.7375
H5 H 0.54107 -0.2969 -0.51321
H6 H 0.55743 -0.04536 -0.50519
N3 N 0.60623 -0.3345 -0.62766

#END
```

**Table S5.** Crystal coordinates for *trans*-antarafacial 4-pyDTDA (from Rietveld refinement).

```
data_trans-antarafacial
_symmetry_cell_setting           monoclinic
_symmetry_space_group_name_H-M   'C 2/c'
_symmetry_Int_Tables_number      15
_space_group_name_Hall           '-C 2yn'
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1 x,y,z
2 -x,y,1/2-z
3 -x,-y,-z
4 x,-y,1/2+z
5 1/2+x,1/2+y,z
6 1/2-x,1/2+y,1/2-z
7 1/2-x,1/2-y,-z
8 1/2+x,1/2-y,1/2+z
_cell_length_a                   15.4378(9)
_cell_length_b                   9.0441(17)
_cell_length_c                   11.3877(4)
_cell_angle_alpha                90.0
_cell_angle_beta                 119.8257(28)
_cell_angle_gamma                90.0
_cell_volume                     1379.36
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
S1 S 0.3403 -0.26706 0.18596
S2 S 0.38686 -0.26529 0.04339
N1 N 0.34292 -0.44495 0.20006
N2 N 0.39689 -0.44298 0.04041
C1 C 0.37044 -0.51386 0.12185
C2 C 0.37314 -0.67621 0.12404
C3 C 0.41958 -0.7532 0.06482
H3 H 0.44882 -0.69881 0.02251
C6 C 0.32987 -0.75604 0.18507
H6 H 0.29725 -0.70793 0.22609
C5 C 0.3351 -0.90545 0.18504
H5 H 0.30567 -0.96221 0.22571
C4 C 0.42532 -0.89865 0.06417
N3 N 0.38367 -0.97335 0.12522
H4 H 0.45419 -0.94932 0.01668

#END
```

**Figure S6.** Crystal packing of *trans*-cofacial 4-pyDTDA.

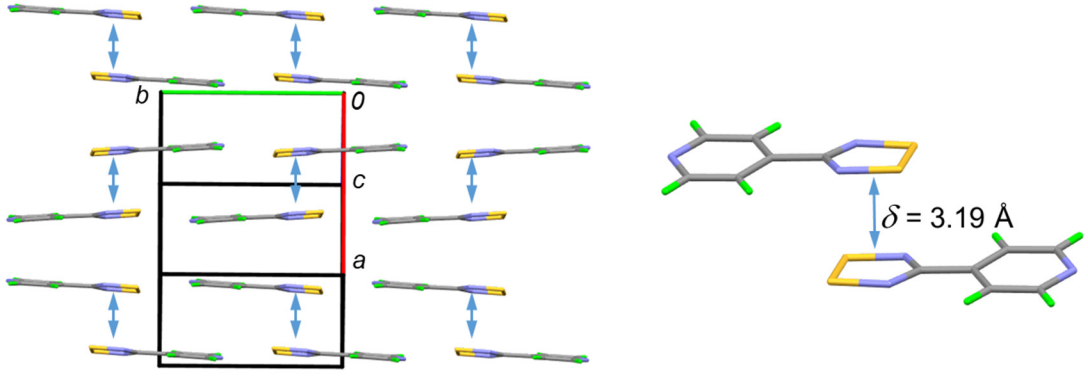



**Figure S7.** Crystal packing of *trans*-antarafacial 4-pyDTDA.