Supplementary Information

Effects of the Peripheral Heteroaryl Substituents on the Photochromism of New Pyridine-Containing Diarylethenes

Guanming Liao, Dandan Xue, Chunhong Zheng, * Renjie Wang and Shouzhi Pu*

Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science and Technology Normal University, 330013 Nanchang, P. R. China

Supplementary data

Figure S1. Absorption spectral changes of 2 and 3 induced by photoirradiation in hexane (2.0 × 10^{-5} mol L^{-1}):
(a) 2; and (b) 3.

*e-mail: articlechem@163.com, pushouzhi@tsinghua.org.cn
**Figure S2.** Fatigue resistances of diarylethenes 1-3 in hexane in air atmosphere at room temperature. Initial absorbance of the sample was fixed at 1.0.

**Figure S3.** Thermal fading of 2c and 3c in hexane at various temperatures: (a) 2c; (b) 3c.

**Figure S4.** Fluorescence spectral changes of 2 and 3 in hexane (5.0 \times 10^{-5}\text{ mol L}^{-1}), excited at 300 nm: (a) 2; and (b) 3.
Figure S5. Packing views along the x direction: (a) 1o; (b) 2o; and (c) 3o.
### Table S1. Crystallographic parameters of 1o-3o

<table>
<thead>
<tr>
<th>Parameter</th>
<th>1o</th>
<th>2o</th>
<th>3o</th>
</tr>
</thead>
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<td>C₂₇H₁₀F₆NS₂</td>
<td>C₂₆H₁₄F₆N₂S₂</td>
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<tr>
<td><strong>Formula weight</strong></td>
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<td>535.55</td>
<td>536.54</td>
</tr>
<tr>
<td><strong>Temperature / K</strong></td>
<td>296(2)</td>
<td>296(2)</td>
<td>296(2)</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
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<td>monoclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P-1</td>
<td>P-1</td>
<td>P2₁/c</td>
</tr>
<tr>
<td><strong>Unit cell dimension</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a / Å</td>
<td>9.4292(10)</td>
<td>8.6153(5)</td>
<td>15.0980(6)</td>
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<tr>
<td>b / Å</td>
<td>11.1096(13)</td>
<td>11.7960(8)</td>
<td>19.4054(8)</td>
</tr>
<tr>
<td>c / Å</td>
<td>13.6106(15)</td>
<td>13.6679(9)</td>
<td>8.4923(4)</td>
</tr>
<tr>
<td>α / degree</td>
<td>90.735(7)</td>
<td>73.315(3)</td>
<td>90.00</td>
</tr>
<tr>
<td>β / degree</td>
<td>106.507(6)</td>
<td>81.381(3)</td>
<td>98.468(2)</td>
</tr>
<tr>
<td>γ / degree</td>
<td>110.045(6)</td>
<td>68.866(2)</td>
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<td><strong>Volume / Å³</strong></td>
<td>1274.6(2)</td>
<td>1239.37(14)</td>
<td>2460.97(18)</td>
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<td><strong>Z</strong></td>
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<td>1</td>
<td>4</td>
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<tr>
<td><strong>Density (calculated) / (g cm⁻³)</strong></td>
<td>1.380</td>
<td>1.435</td>
<td>1.448</td>
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<tr>
<td><strong>Goodness-of-fit on F²</strong></td>
<td>1.126</td>
<td>1.004</td>
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<tr>
<td><strong>Final R index [I/2σ(I)]</strong></td>
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<td>wR2</td>
<td>R1</td>
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<tr>
<td></td>
<td>0.1068</td>
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</table>

Z: Number of chemical formula units per unit cell; F: structure factor; R: discrepancy index.
Figure S6. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 4.
Figure S7. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5.

Figure S8. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 6.
Figure S9. $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of 1o.
Figure S10. $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of 2o.
Figure S11. $^1$H NMR (400 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of 3o.
checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: 140414lgm3_0m

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<td>gamma=110.045(6)</td>
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<td>S = 1.126</td>
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The following ALERTS were generated. Each ALERT has the format test-name_ALERT_alert-type_alert-level. Click on the hyperlinks for more details of the test.
**Alert level C**

ABSTY03_ALERT_1_C The _exptl_absorpt_correction_type has been given as none. However values have been given for Tmin and Tmax. Remove these if an absorption correction has not been applied.

From the CIF: _exptl_absorpt_correction_T_min 0.960
From the CIF: _exptl_absorpt_correction_T_max 0.967

RFACR01_ALERT_3_C The value of the weighted R factor is > 0.25

Weighted R factor given 0.287

PLAT084_ALERT_3_C High wR2 Value (i.e. > 0.25) ................... 0.29 Report

PLAT213_ALERT_2_C Atom F1 has ADP max/min Ratio ..... 3.2 prolat

PLAT234_ALERT_4_C Large Hirshfeld Difference F3’ -- C14 .. 0.17 Ang.

PLAT241_ALERT_2_C High ‘MainMol’ Ueq as Compared to Neighbors of C6 Check

PLAT242_ALERT_2_C Low ‘MainMol’ Ueq as Compared to Neighbors of C13 Check

PLAT340_ALERT_3_C Low Bond Precision on C-C Bonds ............... 0.0067 Ang.

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**Alert level G**

PLAT005_ALERT_5_G No Embedded Refinement Details found in the CIF Please Do!

PLAT066_ALERT_1_G Predicted and Reported Tmin&Tmax Range Identical ? Check

PLAT072_ALERT_2_G SHELXL First Parameter in WGHT Unusually Large 0.16 Report

PLAT093_ALERT_1_G No s.u.’s on H-positions, Refinement Reported as mixed Check

PLAT242_ALERT_2_G Low ‘MainMol’ Ueq as Compared to Neighbors of C14 Check

PLAT242_ALERT_2_G Low ‘MainMol’ Ueq as Compared to Neighbors of C15 Check

PLAT301_ALERT_3_G Main Residue Disorder ................ Percentage = 8 Note

PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 62 Check

PLAT899_ALERT_4_G SHELXL97 is Deprecated and Succeeded by SHELXL 2014 Note

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0 ALERT level A = Most likely a serious problem - resolve or explain
0 ALERT level B = A potentially serious problem, consider carefully
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CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 140302lgm_0m

Bond precision: C-C = 0.0052 Å Wavelength=0.71073

Cell: a=8.6153(5) b=11.7960(8) c=13.6679(9)
alpha=73.315(3) beta=81.381(3) gamma=68.866(2)

Temperature: 296 K

Table:

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<td>-P 1</td>
</tr>
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<tr>
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<td>C27 H19 F6 N S2</td>
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AbsCorr = NONE

Data completeness= 0.982     Theta(max)= 25.000
R(reflections)= 0.0580( 3572)   wr2(reflections)= 0.1728( 4280)

S = 1.004       Npar= 356

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
Alert level B

PLAT230_ALERT_2_B Hirshfeld Test Diff for C3 -- C4 .. 11.0 s.u.

Alert level C

ABSTY03_ALERT_1_C The _exptl_absorpt_correction_type has been given as none. However values have been given for Tmin and Tmax. Remove these if an absorption correction has not been applied.

From the CIF: _exptl_absorpt_correction_T_min 0.942
From the CIF: _exptl_absorpt_correction_T_max 0.952

PLAT220_ALERT_2_C Atom F6 has ADP max/min Ratio ...... 3.1 prolat
PLAT223_ALERT_2_C Atom F5' has ADP max/min Ratio ...... 3.3 prolat
PLAT241_ALERT_2_C Large Non-Solvent C Ueq(max)/Ueq(min) Range 3.8 Ratio
PLAT241_ALERT_2_C High ‘MainMol’ Ueq as Compared to Neighbors of S2 Check
PLAT241_ALERT_2_C High ‘MainMol’ Ueq as Compared to Neighbors of C2 Check
PLAT242_ALERT_2_C Low ‘MainMol’ Ueq as Compared to Neighbors of C3 Check
PLAT242_ALERT_2_C Low ‘MainMol’ Ueq as Compared to Neighbors of C13 Check
PLAT242_ALERT_2_C Low ‘MainMol’ Ueq as Compared to Neighbors of C24 Check
PLAT340_ALERT_3_C Low Bond Precision on C-C Bonds ............... 0.00521 Ang.

Alert level G

PLAT005_ALERT_5_G No Embedded Refinement Details found in the CIF Please Do!
PLAT066_ALERT_1_G Calculated and Reported Z Differ by a Factor ... 2.00 Check
PLAT230_ALERT_2_G Hirshfeld Test Diff for F4 -- C14 .. 13.5 s.u.
PLAT242_ALERT_2_G Low ‘MainMol’ Ueq as Compared to Neighbors of C14 Check
PLAT242_ALERT_2_G Low ‘MainMol’ Ueq as Compared to Neighbors of C15 Check
PLAT301_ALERT_3_G Main Residue Disorder .......... Percentage = 8 Note
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 62 Check
PLAT899_ALERT_4_G SHELXL97 is Deprecated and Succeeded by SHELXL 2014 Note

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12 ALERT type 2 Indicator that the structure model may be wrong or deficient
2 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check
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No syntax errors found. CIF dictionary Interpreting this report

Datablock: 140301lgm_0m

Bond precision:  C-C = 0.0042 A  Wavelength=0.71073

Cell:  
\[a=15.0980(6)\]  \[b=19.4054(8)\]  \[c=8.4923(4)\]  
\[alpha=90\]  \[beta=98.468(2)\]  \[gamma=90\]  
Temperature:  296 K

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\begin{array}{ll}
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\text{Space group} & \text{P 21/c} & \text{P21/c} \\
\text{Hall group} & \text{-P 2ybc} & ? \\
\text{Moiety formula} & \text{C26 H18 F6 N2 S2} & ? \\
\text{Sum formula} & \text{C26 H18 F6 N2 S2} & \text{C26 H18 F6 N2 S2} \\
\text{Mr} & 536.54 & 536.54 \\
\text{Dx, g cm}^{-3} & 1.448 & 1.448 \\
\text{Z} & 4 & 4 \\
\text{Mu (mm}^{-1}) & 0.280 & 0.280 \\
\text{F000} & 1096.0 & 1096.0 \\
\text{F000'} & 1097.65 & \\
\text{h,k,lmax} & 19,25,11 & 19,25,11 \\
\text{Nref} & 5716 & 5695 \\
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\text{Tmin'} & 0.914 & \\
\end{array}
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\[R(\text{reflections})= 0.0566( 4154)\]  
\[\text{wr2}(\text{reflections})= 0.1886( 5695)\]

S = 1.041  
Npar= 328

The following ALERTS were generated. Each ALERT has the format  
\text{test-name ALERT alert-type alert-level}.  
Click on the hyperlinks for more details of the test.
**Alert level C**

ABSTY03_ALERT_1_C  The _exptl_absorpt_correction_type has been given as none. However values have been given for Tmin and Tmax. Remove these if an absorption correction has not been applied.

From the CIF: _exptl_absorpt_correction_T_min  0.916
From the CIF: _exptl_absorpt_correction_T_max  0.931

PLAT220_ALERT_2_C  Large Non-Solvent  C     Ueq(max)/Ueq(min) Range  3.2 Ratio
PLAT220_ALERT_2_C  Hirshfeld Test Diff for  C3  --  C4  ..  6.5 s.u.
PLAT241_ALERT_2_C  High  ‘MainMol’ Ueq as Compared to Neighbors of  S2  Check
PLAT241_ALERT_2_C  ‘MainMol’ Ueq as Compared to Neighbors of  C2  Check
PLAT242_ALERT_2_C  Low  ‘MainMol’ Ueq as Compared to Neighbors of  C15  Check
PLAT242_ALERT_2_C  ‘MainMol’ Ueq as Compared to Neighbors of  C24  Check
PLAT340_ALERT_3_C  Low Bond Precision on  C-C Bonds ..................  0.00423 Ang.

**Alert level G**

PLAT005_ALERT_5_G  No Embedded Refinement Details found  in the CIF  Please Do !
PLAT066_ALERT_1_G  Predicted and Reported Tmin&Tmax Range Identical  ? Check
PLAT072_ALERT_2_G  SHELXL First Parameter in WGHT  Unusually Large  0.10 Report
PLAT093_ALERT_1_G  No s.u.’s on H-positions, Refinement Reported as  mixed Check
PLAT434_ALERT_2_G  Short Inter HL..HL Contact  F2  ..  F4  ..  2.82 Ang.
PLAT899_ALERT_4_G  SHELXL97 is Deprecated and Succeeded by SHELXL  2014 Note

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