Supporting Information

Yellow NIR dye: π-Fused bisbenzoBODIPYs with electron-withdrawing groups

Mitsunori Nakamura,[a] Manami Kitatsuka,[a] Kohtarou Takahashi,[a] Toshi Nagata,[b] Shigeki Mori,[c] Daiki Kuzuhara,[d] Tetsuo Okujima,[a] Hiroko Yamada,[a,d] Takahiro Nakae[a] and Hidemitsu Uno[a,*]

[a] *Department of Chemistry and Biology, Graduate School of Science and Engineering, Ehime University, Matsuyama 790-8577, Japan.*

[b] *National Institutes for Natural Sciences (NINS), Institute for Molecular Science (IMS), 5-1 Higashiyama, Myodaiji, Okazaki 444-8787, Japan; Present address: Applied Chemistry, Faculty of Science and Engineering, Meijo University, Shiogamaguchi 1-501, Tenpaku-ku, Nagoya 468-8502, Japan*

[c] *Integrated Center for Sciences, Ehime University, Matsuyama 790-8577, Japan.*

[d] *Graduate School of Materials Science, Nara Institute of Science and Technology, Ikoma 630-0192, Japan; CREST JST, Chiyoda-ku, 102-0075, Japan*

Time-dependent stability

The UV vessels containing *syn*-**8**, *anti*-**8**, **9** and **10** in $CHCl_3$ were left open under a room luminescent light. The spectra were taken at the indicated time (Figs S1–S4).

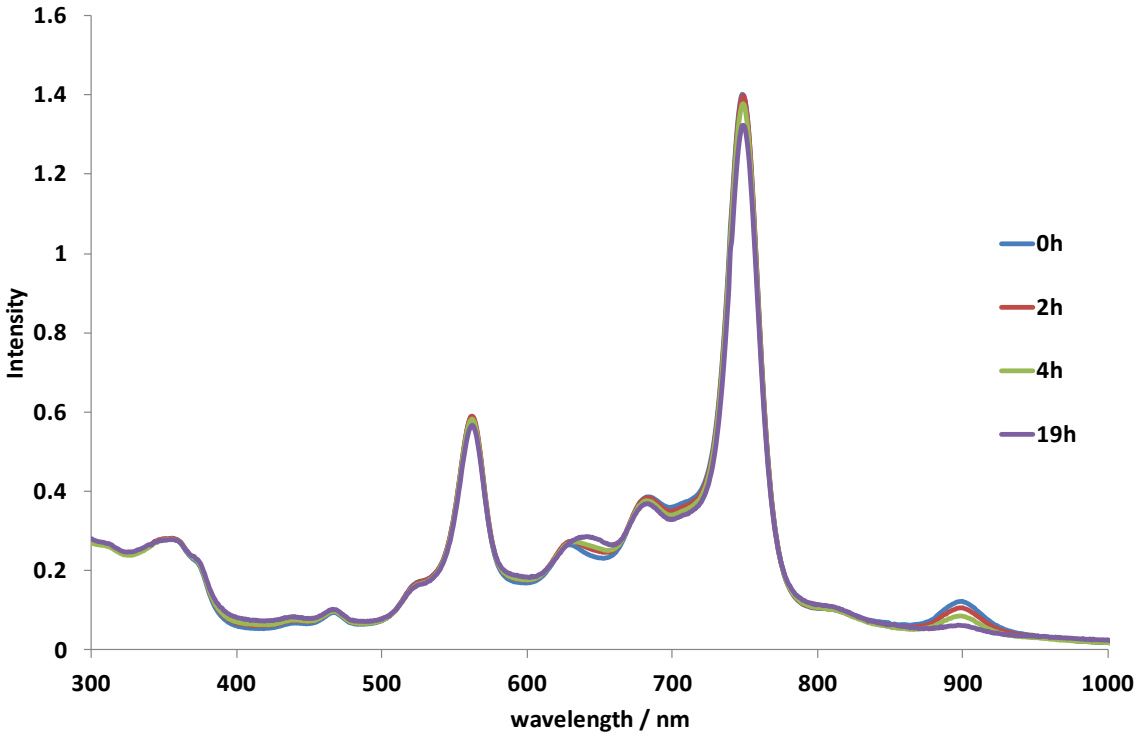


Figure S1. Time-dependent decay experiment of *syn*-**8**

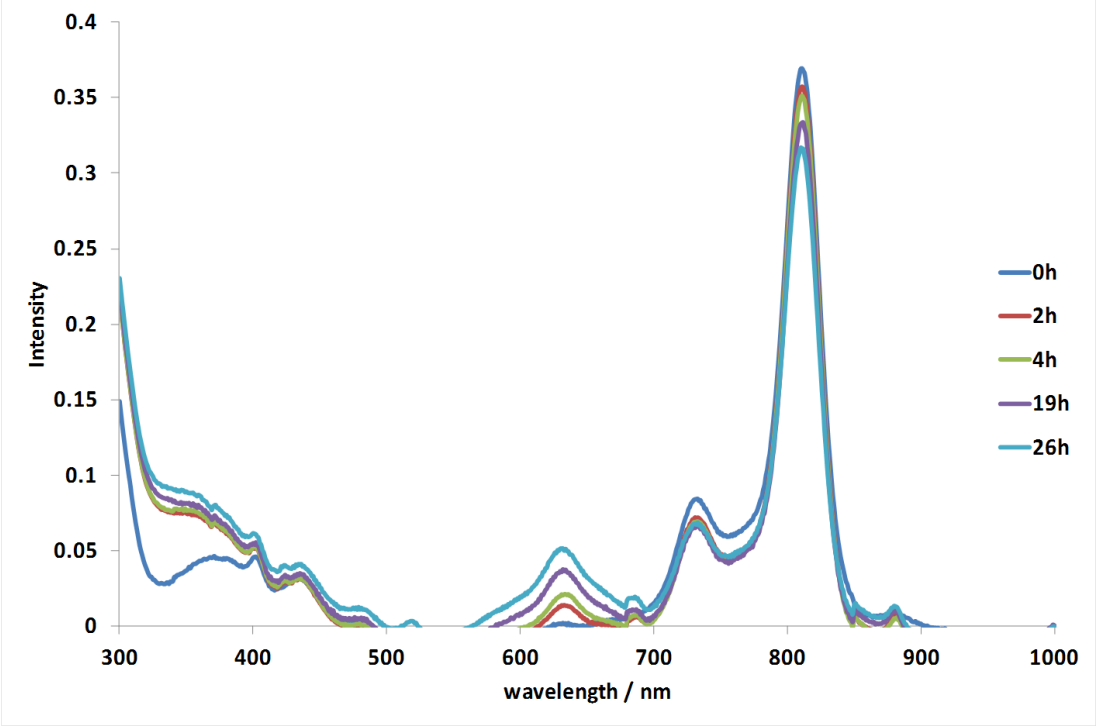


Figure S2. Time-dependent decay experiment of *anti*-**8**

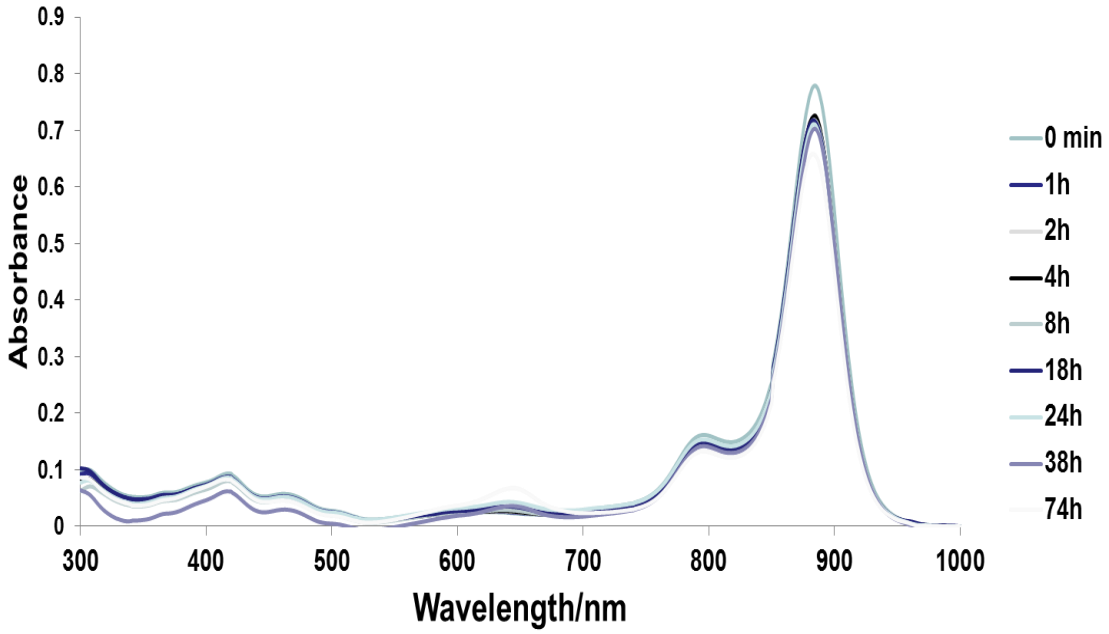


Figure S3. Time-dependent decay experiment of **9**

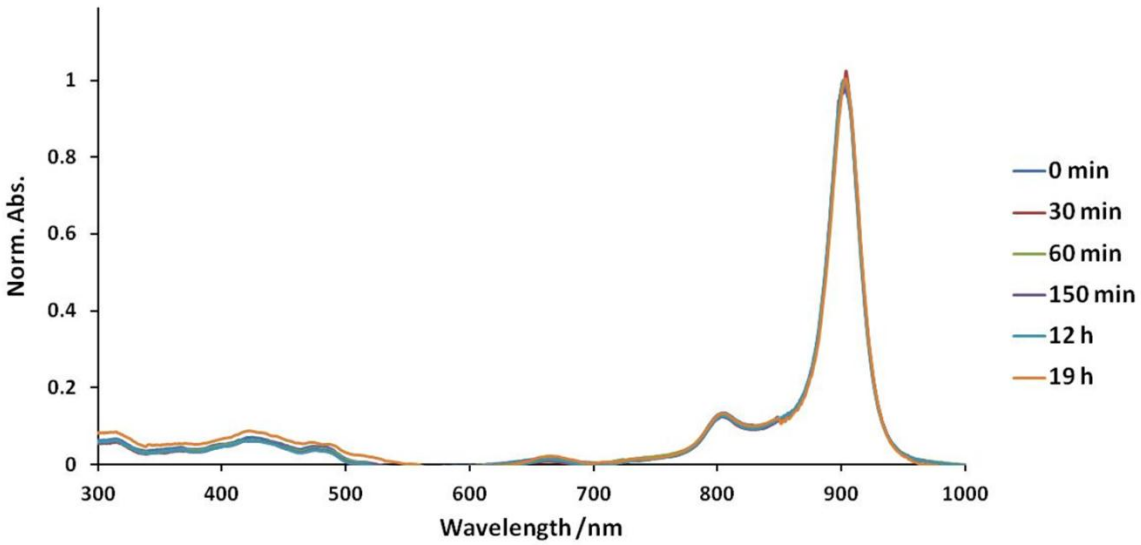


Figure S4. Time-dependent decay experiment of **10**

CV experiment

The voltammogramme of **9** was taken at Pt-Pt electrodes (anode: 0.0201 cm^2) with the sweep rate of 0.1 $V \cdot s^{-1}$ in CH_2Cl_2 containing 0.1 $mol \cdot dm^{-3}$ Bu_4NPF_6, the potential being quoted against Fc/Fc^+. The half-wave potential was 0.44 V, which was calculated to be 0.78 V *vs* SCE.

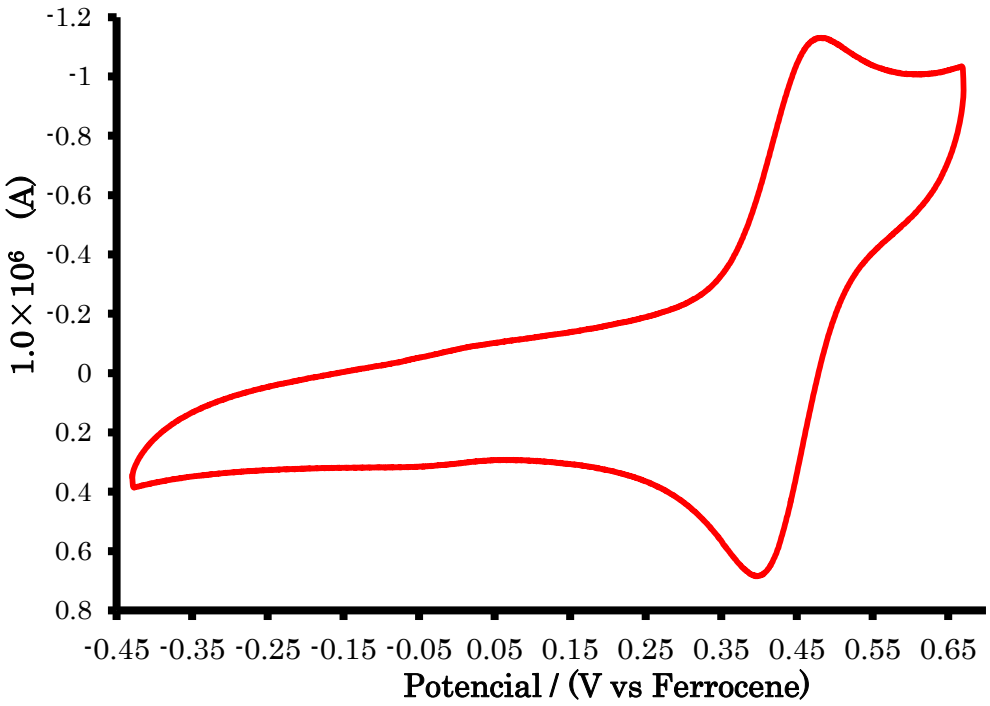
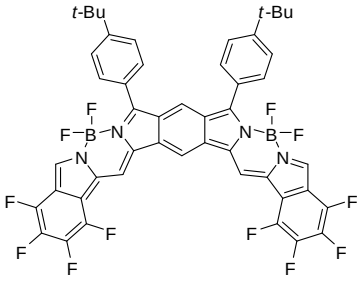
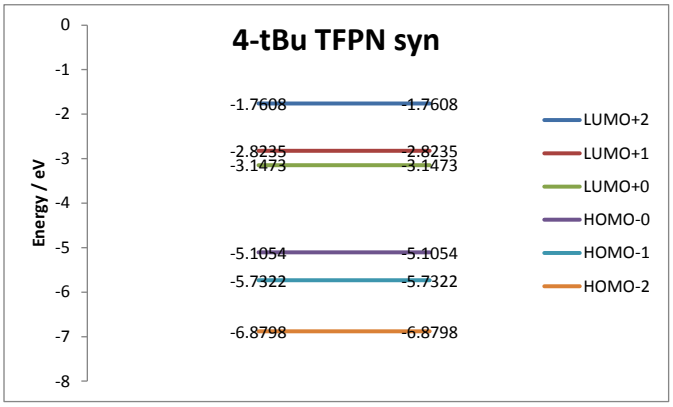
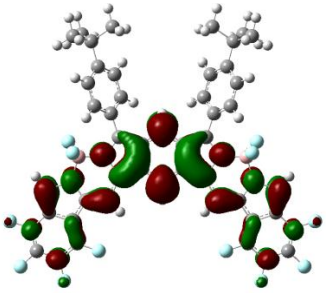


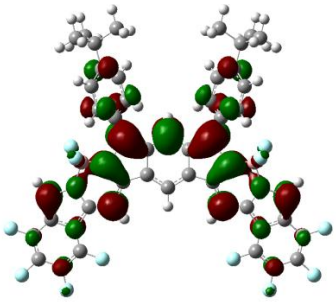
Figure S5. Cyclic voltammogramme of **9**



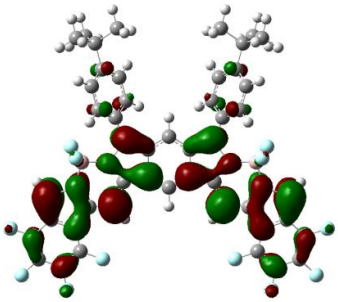




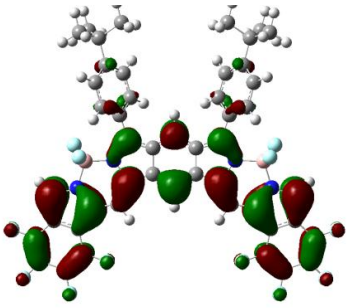
236 LUMO+2 -1.7608eV



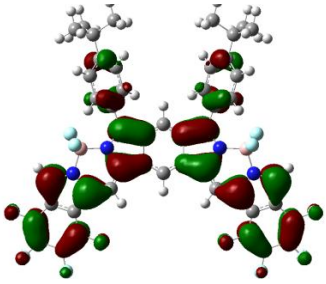
235 LUMO+1 -2.8235eV



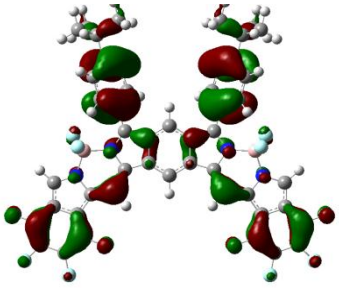
234LUMO+0 -3.1473eV



233 HOMO-0 -5.1054eV

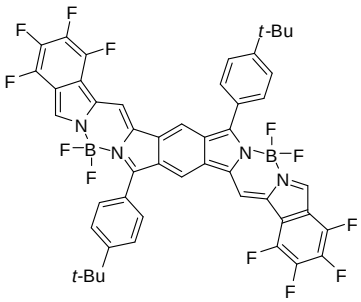


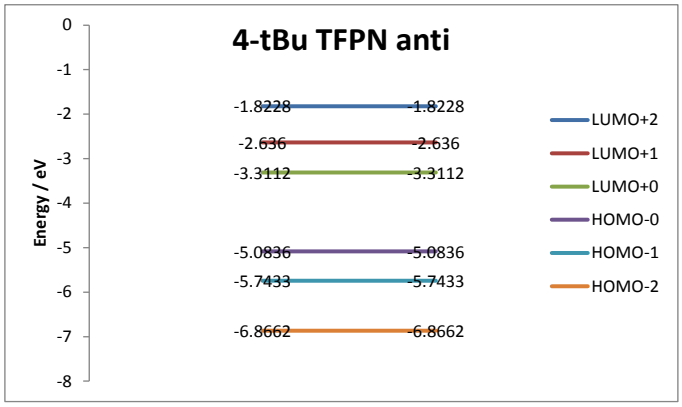
232 HOMO-1 -5.7322eV

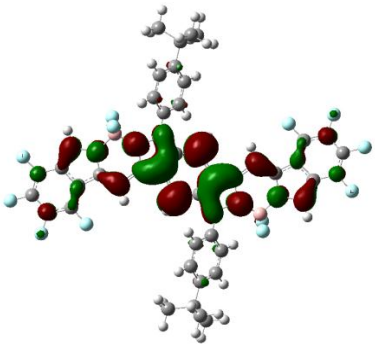


231 HOMO-2 -6.8798eV

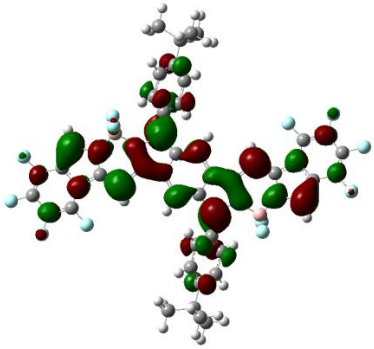
Figure S6. TD-DFT calculation results of *syn*-**8**



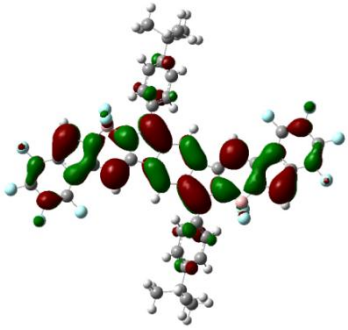




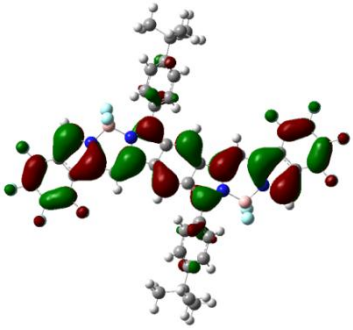
236 LUMO+2 -1.8228eV



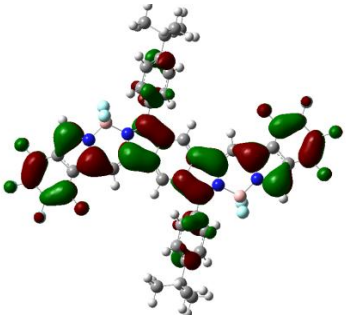
235 LUMO+1 -2.6360eV



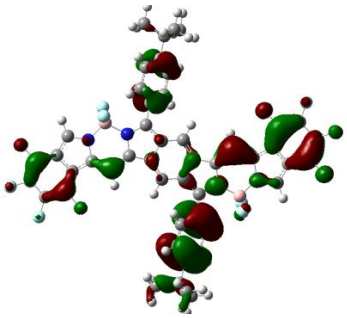
234LUMO+0 -3.3112eV



233 HOMO-0 -5.0836eV



232 HOMO-1 -5.7433eV



231 HOMO-2 -6.8662eV

Figure S7. TD-DFT calculation results of *anti*-**8**

X-ray experiment

Table S1. Crystallographic summary

	syn-**7**[a]	*anti*-**7**·2THF	*syn*-**8**[a]	**14**·$C_2H_4Cl_2$[a]	**16**
crystal formula	$C_{50}H_{36}B_2F_{12}N_4$	$C_{58}H_{52}B_2F_{12}N_4O_2$	$C_{48}H_{32}B_2F_{12}N_4$	$C_{60}H_{52}B_2Cl_2F_4N_8$	$C_{54}H_{40}B_2F_4N_8$
space group	$P2_1/m$	$P2_1/c$	$C2/c$	$P\text{-}1$	$P2_1/c$
a[Å]	9.1240(5)	16.7527(11)	11.4237(3)	10.04744(18)	12.3328(4)
b[Å]	23.4937(12)	15.1798(11)	40.4906(10)	17.2665(4)	26.4067(7)
c[Å]	12.0150(7)	23.1208(15)	21.6705(6)	18.6317(4)	19.8528(6)
α[°]	90	90	90	112.4285(10)	90
β[°]	102.275(8)	117.527(8)	100.521(7)	92.3032(12)	117.1092(18)
γ[°]	90	90	90	104.9867(9)	90
V[Å^3]	2516.6(3)	5214.1(7)	9855.2(5)	2851.06(10)	5755.1(3)
Z	2	4	8	2	4
Radiation	Cu$K\alpha$	Cu$K\alpha$	Cu$K\alpha$	Cu$K\alpha$	Cu$K\alpha$
μ[mm^{-1}]	0.896	0.968	0.901	1.499	0.580
unique reflns	4710	9535	9005	10264	10522
obsd reflns	3315	3566	3857	4875	7248
R_{equiv}	0.0424	0.1002	0.0508	0.0866	0.0524
Parameters (restrained)	404 (505)	949 (1288)	723 (643)	752 (254)	687 (482)
R_1 [I > 2σ(I)]	0.0692	0.0894	0.0739	0.0780	0.0568
wR_2 (All)	0.1972	0.2305	0.2183	0.1963	0.1263
GOF	1.021	1.138	1.056	1.056	1.021
T[K]	100	100	100	100	100
CCDC No	963109	963110	963111	963112	963113

[a] The structures are refined without the indicated molecules by Platon Squeeze.

checkCIF/PLATON (full publication check)

Datablock: *syn*-7

Bond precision: C-C = 0.0041 A Wavelength=1.54187

Cell: a=9.1240(5) b=23.4937(12) c=12.0150(7)

alpha=90 beta=102.275(8) gamma=90

Temperature: 100 K

	Calculated	Reported
Volume	2516.6(3)	2516.6(3)
Space group	P 21/m	P 1 21/m 1
Hall group	-P 2yb	-P 2yb
Moiety formula	C50 H36 B2 F12 N4	C50 H36 B2 F12 N4
Sum formula	C50 H36 B2 F12 N4	C50 H36 B2 F12 N4
Mr	942.45	942.46
Dx,g cm-3	1.244	1.244

Z	2	2
Mu (mm-1)	0.896	0.896
F000	964.0	964.0
F000'	967.69	
h,k,lmax	10,28,14	10,27,14
Nref	4720	4710
Tmin,Tmax	0.870,0.931	0.699,0.931
Tmin'	0.807	

Correction method= MULTI-SCAN

Data completeness= 0.998 Theta(max)= 68.230

R(reflections)= 0.0692(3315) wR2(reflections)= 0.1972(4706)

S = 1.021 Npar= 404

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

PLAT234_ALERT_4_C Large Hirshfeld Difference C24 -- C25 .. 0.18 Ang.

PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor .... 2.2 Note

PLAT340_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.0041 Ang.

PLAT367_ALERT_2_C Long? C(sp?)-C(sp?) Bond C12 - C13 ... 1.57 Ang.

PLAT367_ALERT_2_C Long? C(sp?)-C(sp?) Bond C14 - C15 ... 1.57 Ang.

PLAT906_ALERT_3_C Large K value in the Analysis of Variance ..... 7.850 Check

PLAT906_ALERT_3_C Large K value in the Analysis of Variance ..... 2.215 Check

PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L= 0.600 6

Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 21 Note

PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ... 20

PLAT301_ALERT_3_G Main Residue Disorder ..... Percentage = 29 Note

PLAT605_ALERT_4_G Structure Contains Solvent Accessible VOIDS of . 235 A**3

PLAT793_ALERT_4_G The Model has Chirality at C15 (Verify) R

PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms .... ! Info

PLAT860_ALERT_3_G Number of Least-Squares Restraints ..... 505 Note

PLAT869_ALERT_4_G ALERTS Related to the use of SQUEEZE Suppressed ! Info

PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 4

PLAT961_ALERT_5_G Dataset Contains no Negative Intensities ..... Please Check

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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

8 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight

10 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data

5 ALERT type 2 Indicator that the structure model may be wrong or deficient

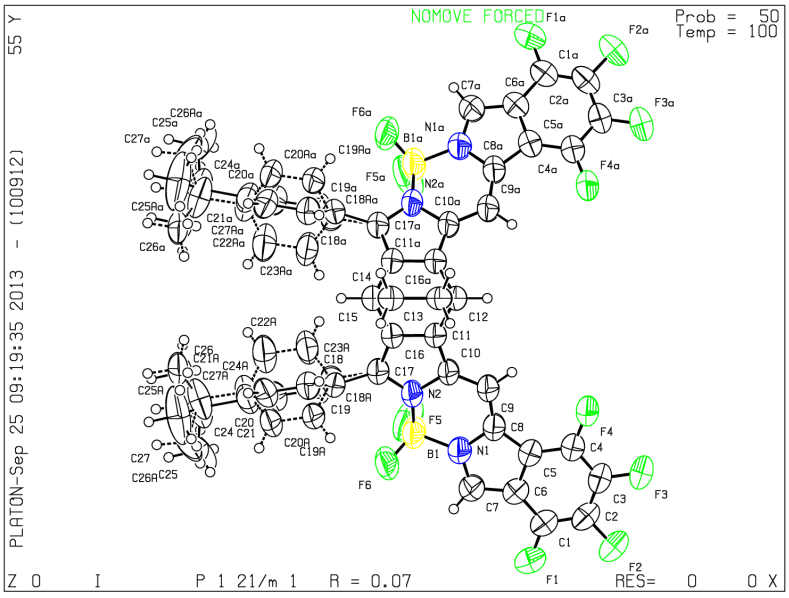
6 ALERT type 3 Indicator that the structure quality may be low

5 ALERT type 4 Improvement, methodology, query or suggestion

2 ALERT type 5 Informative message, check

PLATON version of 18/09/2013; check.def file version of 12/09/2013

Datablock *syn*-7 - ellipsoid plot



Datablock: *anti*-7

Bond precision: C-C = 0.0081 A Wavelength=1.54187

Cell: a=16.7527(11) b=15.1798(11) c=23.1208(15)

alpha=90 beta=117.527(8) gamma=90

Temperature: 100 K

	Calculated	Reported

Volume	5214.1(7)	5214.1(7)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C50 H36 B2 F12 N4, 2(C4 H8 O)	C50 H36 B2 F12 N4, 2(C4 H8 O)
Sum formula	C58 H52 B2 F12 N4 O2	C58 H52 B2 F12 N4 O2
Mr	1086.66	1086.68
Dx,g cm-3	1.384	1.384
Z	4	4
Mu (mm-1)	0.967	0.968
F000	2248.0	2248.0
F000'	2256.33	
h,k,lmax	20,18,27	20,18,27
Nref	9550	9535
Tmin,Tmax	0.873,0.981	0.528,0.981
Tmin'	0.873	

Correction method= MULTI-SCAN

Data completeness= 0.998 Theta(max)= 68.250

R(reflections)= 0.0894(3566) wR2(reflections)= 0.2305(9530)

S = 1.138 Npar= 949

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

PLAT026_ALERT_3_B Ratio Observed / Unique Reflections too Low .... 37 %

Alert level C

PLAT230_ALERT_2_C Hirshfeld Test Diff for F6 -- C16 .. 5.2 su

PLAT340_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.0081 Ang.

PLAT411_ALERT_2_C Short Inter H...H Contact H20 .. H51C .. 2.08 Ang.

PLAT411_ALERT_2_C Short Inter H...H Contact H23 .. H54C .. 2.04 Ang.

PLAT906_ALERT_3_C Large K value in the Analysis of Variance ..... 22.074 Check

And 2 other PLAT906 Alerts

More ...

PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L= 0.600 8

Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 67 Note

PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ... 65

PLAT301_ALERT_3_G Main Residue Disorder ..... Percentage = 29 Note

PLAT302_ALERT_4_G Anion/Solvent Disorder ..... Percentage = 100 Note

PLAT793_ALERT_4_G The Model has Chirality at C9 (Verify) R

PLAT793_ALERT_4_G The Model has Chirality at C23 (Verify) R

PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms .... ! Info

PLAT860_ALERT_3_G Number of Least-Squares Restraints ..... 1288 Note

PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 14

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9 **ALERT level G** = General information/check it is not something unexpected

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5 ALERT type 2 Indicator that the structure model may be wrong or deficient

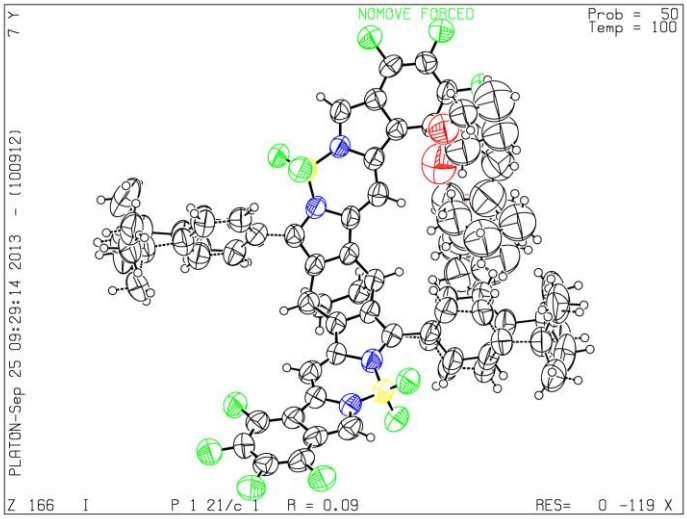
8 ALERT type 3 Indicator that the structure quality may be low

4 ALERT type 4 Improvement, methodology, query or suggestion

1 ALERT type 5 Informative message, check

PLATON version of 18/09/2013; check.def file version of 12/09/2013

Datablock *anti*-7 - ellipsoid plot



Datablock: *syn*-8

Bond precision: C-C = 0.0053 A Wavelength=1.54187

Cell: a=11.4237(3) b=40.4906(10) c=21.6705(6)

alpha=90 beta=100.521(7) gamma=90

Temperature: 100 K

	Calculated	Reported
Volume	9855.2(5)	9855.2(5)
Space group	C 2/c	C 1 2/c 1
Hall group	-C 2yc	-C 2yc
Moiety formula	C48 H32 B2 F12 N4	C48 H32 B2 F12 N4
Sum formula	C48 H32 B2 F12 N4	C48 H32 B2 F12 N4
Mr	914.40	914.41
Dx,g cm-3	1.233	1.232
Z	8	8
Mu (mm-1)	0.900	0.901
F000	3728.0	3728.0
F000'	3742.50	
h,k,lmax	13,48,26	13,48,26
Nref	9039	9005
Tmin,Tmax	0.898,0.973	0.705,0.973
Tmin'	0.898	

Correction method= MULTI-SCAN

Data completeness= 0.996 Theta(max)= 68.240

R(reflections)= 0.0739(3857) wR2(reflections)= 0.2183(9002)

S = 1.056 Npar= 723

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

PLAT026_ALERT_3_C Ratio Observed / Unique Reflections too Low .... 43 %

PLAT230_ALERT_2_C Hirshfeld Test Diff for F5 -- C14 .. 6.7 su

And 2 other PLAT230 Alerts

More ...

PLAT234_ALERT_4_C Large Hirshfeld Difference C32 -- C35A .. 0.20 Ang.

PLAT241_ALERT_2_C High Ueq as Compared to Neighbors for ..... C33 Check

PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor .... 2.6 Note

PLAT340_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.0053 Ang.

PLAT906_ALERT_3_C Large K value in the Analysis of Variance ..... 133.287 Check

And 5 other PLAT906 Alerts

More ...

PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L= 0.600 6

Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 30 Note

PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ... 28

PLAT301_ALERT_3_G Main Residue Disorder ..... Percentage = 21 Note

PLAT434_ALERT_2_G Short Inter HL..HL Contact F4 .. F5 . 2.69 Ang.

PLAT434_ALERT_2_G Short Inter HL..HL Contact F4 .. F12 . 2.82 Ang.

PLAT605_ALERT_4_G Structure Contains Solvent Accessible VOIDS of . 329 A**3

PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms .... ! Info

PLAT860_ALERT_3_G Number of Least-Squares Restraints ..... 643 Note

PLAT869_ALERT_4_G ALERTS Related to the use of SQUEEZE Suppressed ! Info

PLAT910_ALERT_3_G Missing # of FCF Reflections Below Th(Min) ..... 1 Why ?

PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 30

PLAT961_ALERT_5_G Dataset Contains no Negative Intensities ..... Please Check

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0 **ALERT level B** = A potentially serious problem, consider carefully

15 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight

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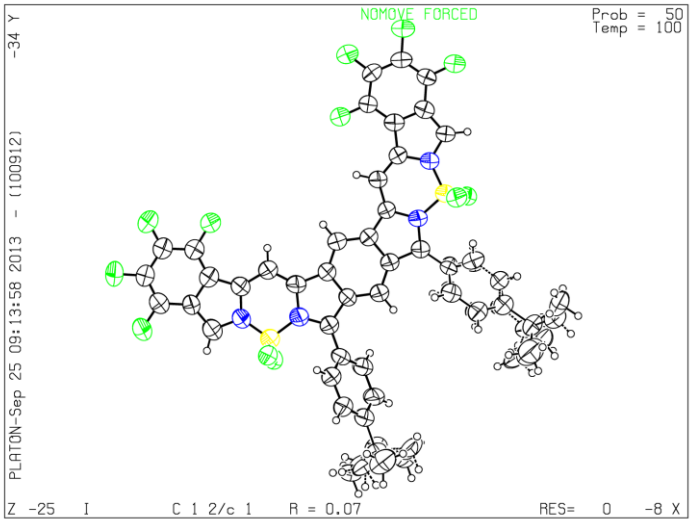
12 ALERT type 3 Indicator that the structure quality may be low

4 ALERT type 4 Improvement, methodology, query or suggestion

2 ALERT type 5 Informative message, check

PLATON version of 18/09/2013; check.def file version of 12/09/2013

Datablock *syn*-8 - ellipsoid plot



Datablock: 14·$C_2H_4Cl_2$

Bond precision: C-C = 0.0057 A Wavelength=1.54187

Cell: a=10.04744(18) b=17.2665(4) c=18.6317(4)
alpha=112.4285(10) beta=92.3032(12) gamma=104.9867(9)

Temperature: 100 K

	Calculated	Reported
Volume	2851.07(11)	2851.06(10)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C58 H48 B2 F4 N8, C2 H4 Cl2	C58 H48 B2 F4 N8, C2 H4 Cl2
Sum formula	C60 H52 B2 Cl2 F4 N8	C60 H52 B2 Cl2 F4 N8
Mr	1053.62	1053.64
Dx,g cm-3	1.227	1.227
Z	2	2
Mu (mm-1)	1.499	1.499
F000	1096.0	1096.0
F000'	1100.56	
h,k,lmax	12,20,22	12,20,22
Nref	10432	10264
Tmin,Tmax	0.882,0.956	0.732,0.956
Tmin'	0.730	

Correction method= MULTI-SCAN

Data completeness= 0.984 Theta(max)= 68.250

R(reflections)= 0.0780(4875) wR2(reflections)= 0.1963(10257)

S = 1.056 Npar= 752

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

PLAT026_ALERT_3_C Ratio Observed / Unique Reflections too Low .... 47 %

PLAT230_ALERT_2_C Hirshfeld Test Diff for C10 -- C11 .. 6.0 su

PLAT234_ALERT_4_C Large Hirshfeld Difference C48 -- C50A .. 0.17 Ang.

PLAT234_ALERT_4_C Large Hirshfeld Difference C48 -- C51A .. 0.23 Ang.

PLAT242_ALERT_2_C Low Ueq as Compared to Neighbors for ..... C48 Check

PLAT340_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.0057 Ang.

PLAT412_ALERT_2_C Short Intra XH3 .. XHn H46 .. H51D .. 1.88 Ang.

Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 16 Note

PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ... 14

PLAT301_ALERT_3_G Main Residue Disorder ..... Percentage = 15 Note

PLAT302_ALERT_4_G Anion/Solvent Disorder ..... Percentage = 100 Note

PLAT605_ALERT_4_G Structure Contains Solvent Accessible VOIDS of . 329 A**3

PLAT793_ALERT_4_G The Model has Chirality at C19 (Verify) S

PLAT793_ALERT_4_G The Model has Chirality at C22 (Verify) S

PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms .... ! Info

PLAT860_ALERT_3_G Number of Least-Squares Restraints ..... 254 Note

PLAT869_ALERT_4_G ALERTS Related to the use of SQUEEZE Suppressed ! Info

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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

7 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight

10 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data

5 ALERT type 2 Indicator that the structure model may be wrong or deficient

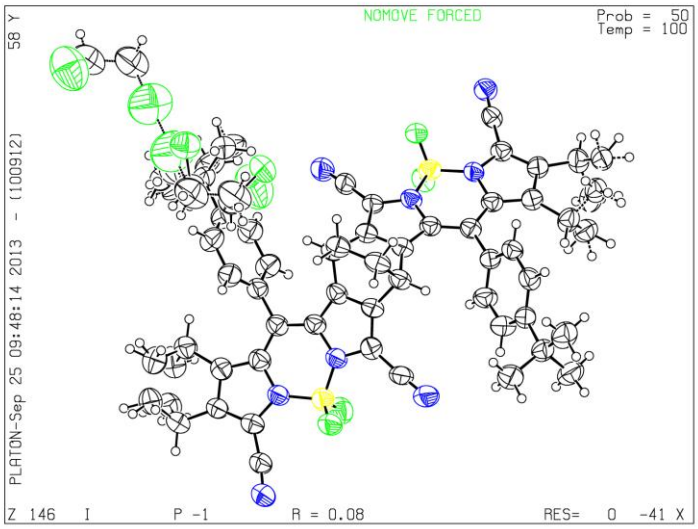
4 ALERT type 3 Indicator that the structure quality may be low

7 ALERT type 4 Improvement, methodology, query or suggestion

1 ALERT type 5 Informative message, check

PLATON version of 18/09/2013; check.def file version of 12/09/2013

Datablock 14·$C_2H_4Cl_2$ - ellipsoid plot



Datablock: 16

Bond precision: C-C = 0.0027 A Wavelength=1.54187

Cell: a=12.3328(4) b=26.4067(7) c=19.8528(6)

alpha=90 beta=117.1092(18) gamma=90

Temperature: 100 K

	Calculated	Reported
Volume	5755.1(3)	5755.1(3)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C54 H40 B2 F4 N8	C54 H40 B2 F4 N8
Sum formula	C54 H40 B2 F4 N8	C54 H40 B2 F4 N8
Mr	898.56	898.58
Dx,g cm-3	1.037	1.037
Z	4	4
Mu (mm-1)	0.580	0.580
F000	1864.0	1864.0
F000'	1869.77	
h,k,lmax	14,31,23	14,31,23

Nref	10525	10522
Tmin,Tmax	0.890,0.955	0.815,0.955
Tmin'	0.890	

Correction method= MULTI-SCAN

Data completeness= 1.000 Theta(max)= 68.240

R(reflections)= 0.0568(7248) wR2(reflections)= 0.1263(10513)

S = 1.021 Npar= 687

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

PLAT213_ALERT_2_C Atom C53A has ADP max/min Ratio ..... 3.9 prolat

PLAT220_ALERT_2_C Large Non-Solvent C Ueq(max)/Ueq(min) ... 3.3 Ratio

PLAT234_ALERT_4_C Large Hirshfeld Difference C47 -- C50A .. 0.17 Ang.

PLAT906_ALERT_3_C Large K value in the Analysis of Variance ..... 6.741 Check

PLAT906_ALERT_3_C Large K value in the Analysis of Variance ..... 2.046 Check

PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L= 0.600 12

Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 23 Note

PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ... 20

PLAT301_ALERT_3_G Main Residue Disorder ..... Percentage = 15 Note

PLAT606_ALERT_4_G VERY LARGE Solvent Accessible VOID(S) in Structure ! Info

PLAT793_ALERT_4_G The Model has Chirality at C19 (Verify) R

PLAT793_ALERT_4_G The Model has Chirality at C22 (Verify) R

PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms .... ! Info

PLAT860_ALERT_3_G Number of Least-Squares Restraints ..... 482 Note

PLAT869_ALERT_4_G ALERTS Related to the use of SQUEEZE Suppressed ! Info

PLAT961_ALERT_5_G Dataset Contains no Negative Intensities ..... Please Check

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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

6 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight

10 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data

4 ALERT type 2 Indicator that the structure model may be wrong or deficient

5 ALERT type 3 Indicator that the structure quality may be low

5 ALERT type 4 Improvement, methodology, query or suggestion

2 ALERT type 5 Informative message, check

PLATON version of 18/09/2013; check.def file version of 12/09/2013

Datablock 16 - ellipsoid plot