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Supporting Information

Synthesis and Optophysical Properties of Novel Dimeric Aza-BODIPY Dyes with a Push-Pull Benzodipyrrolidones Core

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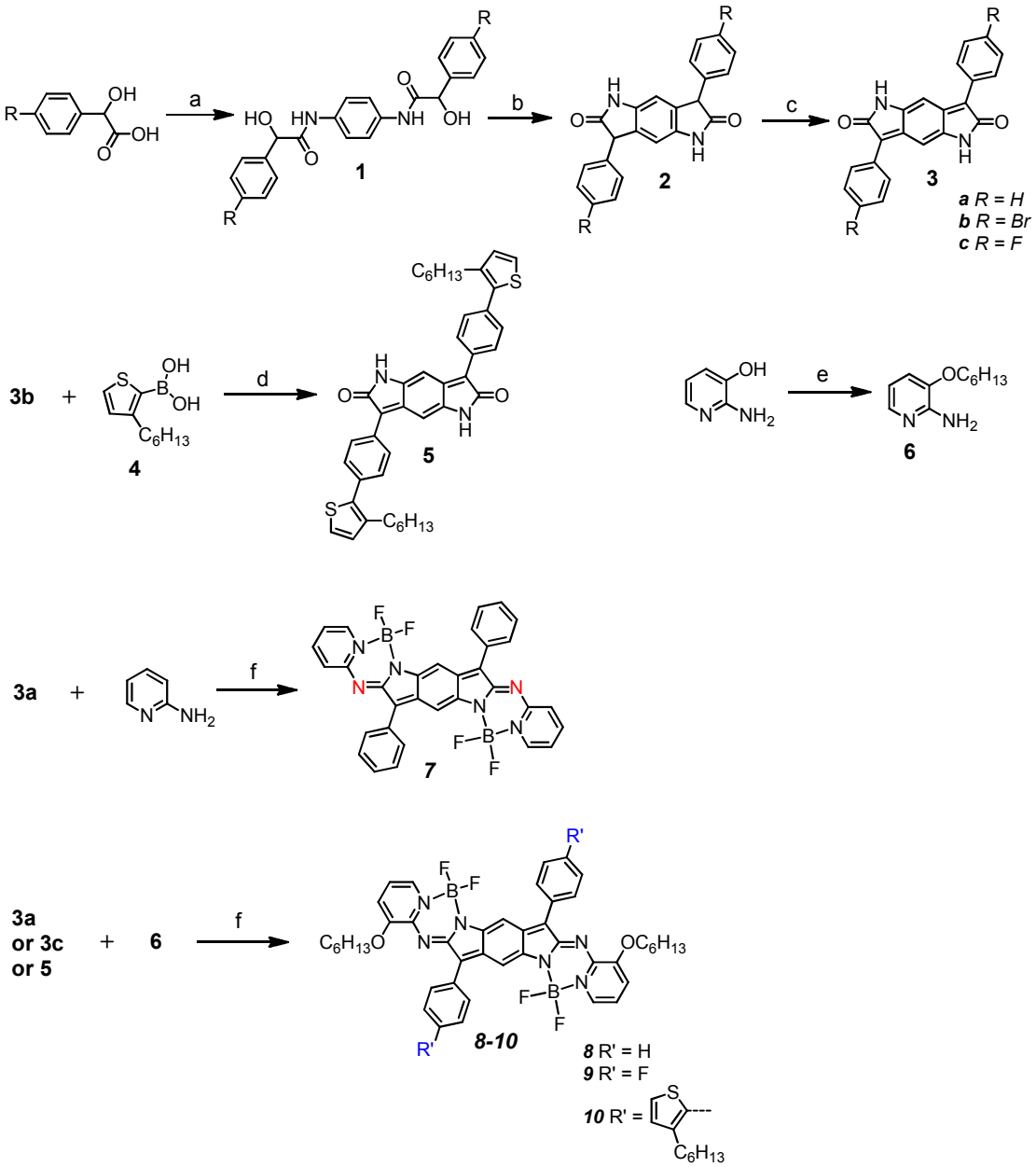
Contents:

I. Experimental Section

General methods:

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 250 Spectrometer. Mass spectra were recorded with a Finnigan MAT and VG Instruments ZAB 2-SE-FPD. UV/Vis spectra were recorded at room temperature on a Perkin-Elmer Lambda 900 spectrometer with dichloromethane as solvent. The redox properties of compounds **7**-**10** were measured with cyclic voltammetry (CV, $[Bu_4NPF_6]$ = 0.1 M, 100 mVs^{-1}) in deoxygenated THF solution at room temperature using a three-electrode electrochemical cell with Bu_4NPF_6 (0.1 M). Cyclic voltammetry for electrochemistry experiments was carried out with an EG&G Princeton Applied Research potentiostat, model 273. The working electrode consisted of a platinum disk (1.5 mm diameter). A platinum wire was used as the counter electrode and an Ag wire was used as the reference electrode internally calibrated with ferrocene/ferrocenium (Fc/Fc^{+}) in the measurement. Compound **3a**, **3b** and **4** were reported by the literature.[1,2] Crystal-structure determinations were carried out on a Nonius KCCD diffractometer with graphite monochromated Mo K radiation. The structures were solved by direct methods (SHELXS-97). Melting points were determined on a Büchi Melting Point B-545 apparatus.



Scheme S1. Synthetic route of *aza*-BODIPY dyes **7-10**. a) benzene-1,4-diamine, chlorobenzene, 130°C, 20 h; b) H_2SO_4, rt., 24 h; c) NaOH, $K_2S_2O_8/H_2O$, ethanol, 90°C, 2 h; d) $Pd(PPh_3)_4$, 2 M K_2CO_3, THF, reflux, 6 h; e) 1-bromohexane, NaH, DMF, rt., 24 h; f) i. $TiCl_4$, Et_3N, Toluene, reflux, 12 h; ii. BF_3•Et_2O, reflux, 4h.

Compound 1c

A mixture of *p*-fluoromandelic acid (2.50 g, 14.69 mmol) and *p*-phenylenediamine (0.53 g, 4.90 mmol) in chlorobenzene was heated to 130 ^{o}C for 20 h. The precipitate was filtered, washed with ethanol and dried in vacuo to get compound **1c** as a grey solid (1.60 g. Yield, 79%).^{1}H NMR (*d*-DMSO, 250 MHz, 298K): δ = 9.89 (s, 2H), 7.60 (s, 4H), 7.57 (m, 4H), 7.22 (t, 4H), 6.48 (d, J = 5.0 Hz, 2H), 5.10 (d, J = 5.0 Hz, 2H). ^{13}C NMR (*d*-DMSO, 62.5 MHz, 298K): δ = 170.7, 163.54, 159.67, 137.09, 134.15, 128.53, 128.4, 119.92, 114.99, 114.65, 73.16.

Compound 2c

Compound **1c** (1.40 g, 3.39 mmol) was added to sulfuric acid (25 mL) and stirred for 24 h at room. Then, the mixture was poured into ice water. The precipitate was filtered, washed with water and dried to get compound **2** as a grey solid (1.20 g. Yield, 94%).^{1}H NMR (*d*-DMSO, 250 MHz, 298K): δ = 10.37 (s, 2H), 7.23 (m, 8H), 6.99 (s, 2H), 7.81(d, J = 5.0 Hz, 2H). ^{13}C NMR (*d*-DMSO, 62.5 MHz, 298K): δ = 176.61, 163.25, 159.39, 137.18, 133.81, 130.17, 129.52, 115.68, 115.34, 106.88, 51.31.

Compound 3c

Sodium hydroxide solution (5 M, 0.50 mL) was dropwised to a suspension of compound **2** (1.20 g, 3.19 mmol) in ethanol. Then potassium persulfate (0.86 g, 3.2 mmol) in water (3 mL) was added. The mixture was heated at reflux for 2 h. The precipitate was filtered, washed with water and ethanol, dried to yield compound 3 as a red solid (0.83 g. Yield, 70%).^{1}H NMR (*d*-DMSO, 250 MHz, 298K): δ = 10.33 (s, 2H), 7.75 (m, 4H), 7.40 (t, 4H), 6.36 (s, 2H). 13C NMR (d-DMSO, 62.5 MHz, 298K): δ = 170.34, 164.20, 160.26, 142.66, 134.64, 131.57, 127.33, 125.72, 115.95, 115.61, 97.62.

Compound 5

In 100 mL two-neck round bottle flask, a mixture of compound **3b** (0.40 g, 0.81mmol), compound **4** (0.52 g, 1.77 mmol), $Pd(PPh_3)_4$ (46.6 mg, 0.04 mmol) and 2 M K_2CO_3 (10 mL) was refluxed in THF for 6 h under argon. The reaction mixture was poured into water and extracted with dichloromethane. After removed the solvent, the crude product was washed with a lot of methanol and a red solid was achieved. The compound was used to the next step without further purification.

Compound 6

A mixture of 2-aminopyridin-3-ol (5.0 g, 45.50 mmol) and NaH (1.50 g, 68.20 mmol) was stirred in DMF at room temperature for 1 h under Ar. Then a solution of 1-bromohexane (8.95 g, 54.60 mmol) in DMF was added and the reaction mixture was stirred for 24 h at room temperature. The reaction mixture was poured into water and extracted with chloroform. The crude product was purified by flash chromatography (petroleum ether/ethyl acetate, 4:1) to afford grey white solid (4.0 g, 46%).^{1}H NMR ($CDCl_3$, 250 MHz, 298K): δ = 7.64 (d, J = 6.5 Hz, 1H), 6.9 (d, J = 7.5 Hz, 1H), 6.62 (m, 1H), 4.74 (s, 2H), 3.99 (t, 2H), 1.86 (m, 2H), 1.49 (m, 6H), 0.93 (t, 3H). ^{13}C NMR ($CDCl_3$, 62.5 MHz, 298K): δ = 150.10, 141.91, 137.99, 116.02, 113.63, 68.15, 31.55, 29.07, 25.76, 22.59, 14.04.

Compound 7-10

General synthetic procedure:

1 equiv of compound **3** (or **5**) and 10 equiv of compound **6** (or pyridin-2-amine) were refluxed in a dry toluene under Ar. To the solution, 15 equiv of titanium tetrachloride and 40 equiv of triethylamine were added and the reaction mixture was refluxed overnight. Then 30 equiv of borontrifluoride etherate was added, and the reaction mixture was refluxed for 4 h. Then the solution was poured into water, and the organic phase was extracted with chloroform. The organic layer was dried over sodium sulfate and the solvent was removed. The crude product was purified by flash chromatography with dichloromethane.

7, Yield: 10.3 %. Melting point: > 380 ^{o}C. ^{1}H NMR (CD_2Cl_2, 250 MHz, 298K): δ = 8.37 (d, J = 5 Hz, 5H), 8.04 (m, 10H), 7.20 (t, 5 H). ^{13}C NMR (CD2Cl2, 62.5 MHz, 298K): δ = 157.65, 154.54, 152.93, 142.86, 141.51, 140.01, 136.23, 119.39, 116.80, 106.30, 102.21. MALDI-TOF-MS (m/z): 587.07.

8, Yield: 5.2 %. Melting point: > 380 ^{o}C. ^{1}H NMR (CD_2Cl_2, 250 MHz, 298K): δ = 8.0 (d, J = 7.5 Hz, 6H), 7.61 (m, 6H), 7.43 (t, 2 H), 7.27 (t, 2H), 7.1 (s, 2H), 4.19 (t, 4H), 1.96 (m, 4H), 1.44 (m, 12H), 1.0 (m, 6H). ^{13}C NMR (CD_2Cl_2, 62.5 MHz, 298K): δ = 147.92, 145.86, 136.41, 131.77, 130.98, 130.08, 129.52, 128.87, 121.90, 119.65, 105.02, 70.25, 31.95, 29.30, 26.02, 23.08, 14.29. MALDI-TOF-MS (*m*/*z*): 788.48.

9, Yield: 6.7 %. Melting point: > 380 ^{o}C. ^{1}H NMR (CD_2Cl_2, 250 MHz, 298K): δ = 8.04 (m, 6H), 7.43 (d, J = 7.5 Hz, 4H), 7.31 (m, 6 H), 7.06 (s, 2H), 4.17 (t, 4H), 1.97 (m, 4H), 1.47 (m, 12H), 1.0 (t, 6H). ^{13}C NMR (CD_2Cl_2, 62.5 MHz, 298K): δ = 161.82, 157.21, 151.54, 145.78, 138.60, 132.97., 132.44, 130.07, 119.78., 116.57, 116.13, 115.79, 110.02, 104.76, 70.21, 31.93, 29.31, 26.03, 23.08, 14.24. MALDI-TOF-MS (*m*/*z*): 824.42.

10, Yield: 7.5 %. Melting point: 328-330 ^{o}C. ^{1}H NMR (CD_2Cl_2, 250 MHz, 298K): δ = 8.10 (d, J = 7.5 Hz, 4H), 8.01 (d, J = 5.0 Hz, 2H), 7.67 (d, J = 7.5 Hz, 4H), 7.44 (d, J = 10.0 Hz, 2 H), 7.37 (d, J = 5.0 Hz, 2H), 7.28 (t, 2H), 7.18 (s, 2H), 7.11 (d, J = 5.0 Hz, 2H) 4.19 (t, 4H), 2.86 (t, 4H), 1.99 (m, 4H), 1.76 (m, 6H), 1.62 (m, 22H), 0.96 (m, 12). ^{13}C NMR (CD_2Cl_2, 62.5 MHz, 298K): δ = 162.03, 152.09, 150.75, 150.16, 149.47, 147.86, 145.86, 139.90, 137.63, 136.19, 134.22, 131.10, 130.81, 130.25, 130.07, 129.61, 125.65, 124.68, 121.82, 119.68, 105.11, 70.19, 32.15, 31.94, 31.47, 29.69, 29.29, 26.07, 23.14, 23.05, 14.24. MALDI-TOF-MS (*m*/*z*): 1120.85.

References

1. W. Cui, J. Yuen and F. Wudl, *Macromolecules*, 2011, **44**, 7869.
2. H. Pan, Y. Li, Y. Wu, P. Liu, B. S. Ong, S. Zhu, and G. Xu, *J. Am. Chem. Soc.,* 2007, **129**, 4112.

Table S1. Electrochemical properties and DFT results of *aza*-BODIPY **7-10**

Compound	[a]E_{ox1}	[a]E_{red1}	[a]*HOMO*	[a]*LUMO*	[b]E_g^{opt}	[c]*HOMO*	[c]*LUMO*	[c]E_g^{cal}
	V	*V*	*eV*	*eV*	*eV*	*eV*	*eV*	*eV*
7	0.63	-0.80	-5.43	-4.00	1.97	-5.639	-3.553	2.086
8	0.60	-0.70	-5.40	-4.10	1.79	-5.365	-3.381	1.984
9	0.60	-0.67	-5.40	-4.13	1.72	-5.489	-3.508	1.981
10	0.52	-0.68	-5.32	-4.12	1.68	-5.357	-3.428	1.929

[a] *electrochemical data was determined by cyclic voltammetric measurement in 0.1 M solution of* Bu_4NPF_6 *in THF: vs* Fc/Fc^+. *Estimated vs vacuum level from* $E_{HOMO} = -4.80\ eV + E_{ox1}$; $E_{LUMO} = -4.80\ eV - E_{red1}$.

[b] *the optical bandgap(* $E_g^{opt} = 1240/\lambda_{onset}$*) was evaluated via absorption onset.*

[c] *the data were obtained from theory calculation based on DFT calculation at the B3LYP/6-31G(d) level.*

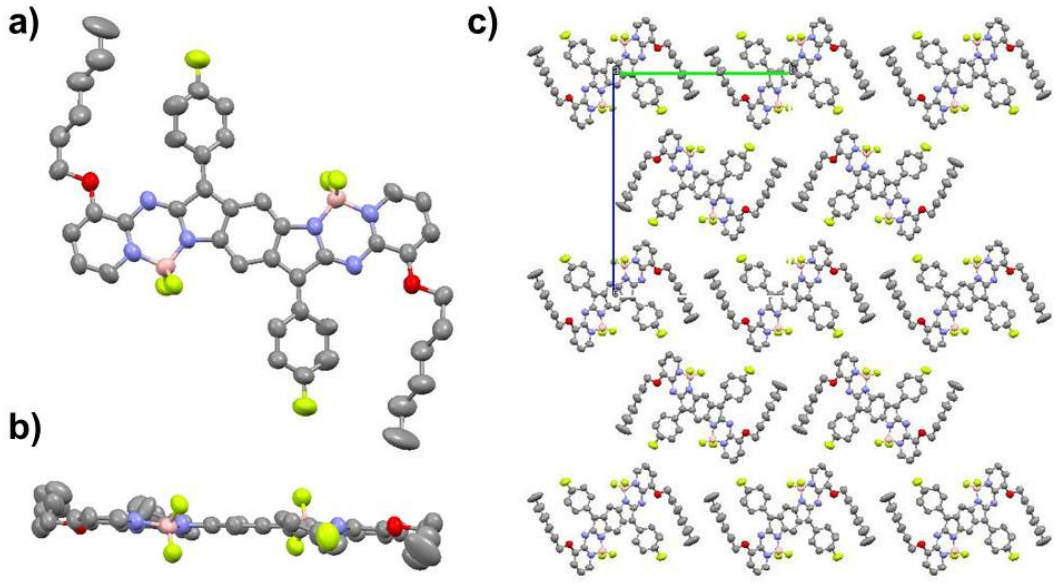


Figure S1. X-ray crystal structures of **9** (a: top view, b: side view). Displacement ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity; c: Packing view down the *a* direction. C, gray; O, red; N, blue; B. pink; F, green.

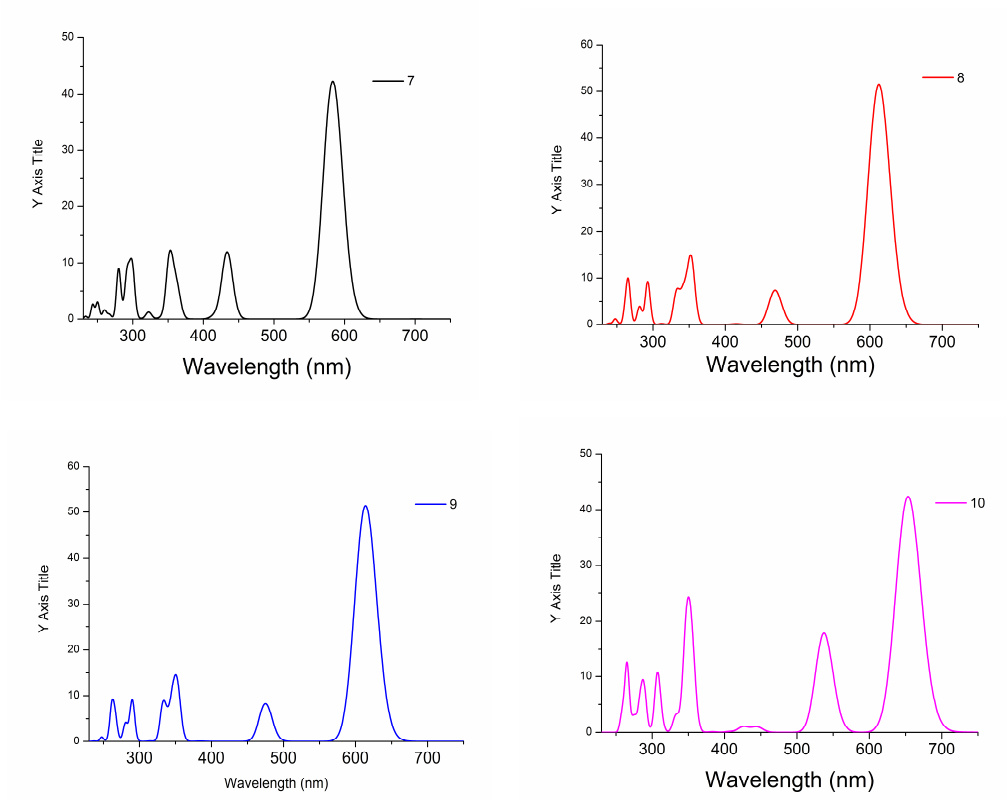


Figure S2. The UV/Vis absorption spectra of **7-10** calculated by B3LYP/6-31G(d) level of theory.

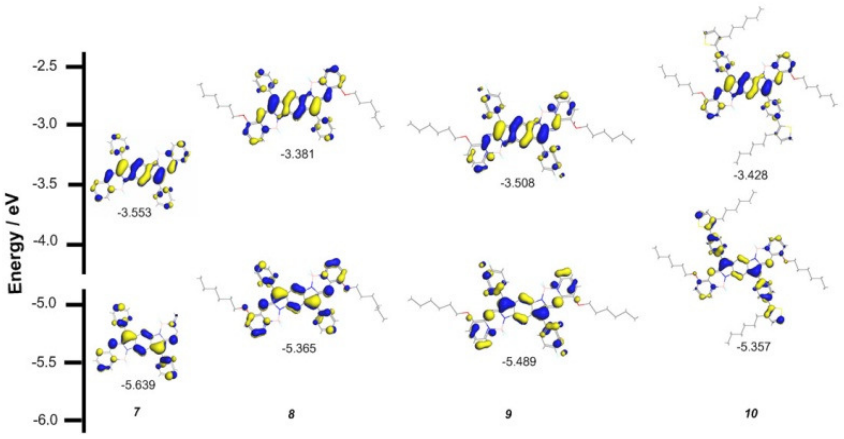


Fig. S3 HOMO and LUMO distributions of *aza*-BODIPYs **7-10** calculated at the B3LYP/6-31G (d) level.

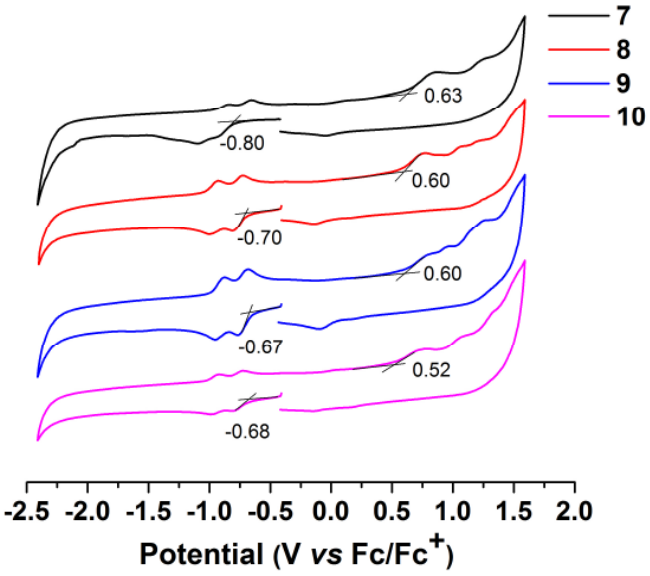


Figure S4. Cyclic voltammograms curves of *aza*-BODIPYs **7-10** in THF (10^{-3} mol L^{-1}); scan rate 100 mVs^{-1}, vs Fc/Fc^{+}.

Crystal data for *aza*-BODIPY 8

formula	$C_{44}H_{44}B_2F_4N_6O_2$
molecular weight	786.5 $gmol^{-1}$
absorption	μ = 0.1 mm^{-1}
crystal size	0.18 x 0.3 x 0.8 mm^3 brown block
space group	P -1 (triclinic)
lattice parameters	a = 11.4702(6)Å α = 113.625(4)°
(calculate from	b = 13.1470(6)Å ß = 95.348(4)°
18532 reflections with	c = 14.9642(8)Å γ = 105.167(4)°
2.6° < θ < 28.4°)	V = 1944.8(2)$Å^3$ z = 2 F(000) = 824
temperature	-80°C
density	d_{xray} = 1.343 gcm^{-3}

data collection

diffractometer	STOE IPDS 2T
radiation	Mo-K_α Graphitmonochromator
Scan – type	ω scans
Scan – width	1°
scan range	2° ≤ θ < 28°
	-15 ≤ h ≤ 15 -17 ≤ k ≤ 17 -16 ≤ l ≤ 19
number of reflections:	
measured	19662
unique	9507 (R_{int} = 0.0946)
observed	5494 (|F|/σ(F) > 4.0)

daten correction, structure solution and refinement

corrections	Lorentz and polarisation correction.
Structure solution	Program: SIR-97 (Direct methods)
refinement	Program: SHELXL-97 (full matrix). 525 refined parameters, weighting scheme: $w=1/[\sigma^2(F_o^2) + (0.103*P)^2+*P]$ with $(Max(F_o^2,0)+2*F_c^2)/3$. H-atoms at calculated positions and refined with isotropic displacement parameters, non H- atoms refined anisotropically.
R-values	wR2 = 0.1794 (R1 = 0.0603 for observed reflections, 0.1031 for all reflections)
goodness of fit	S = 0.909
maximum deviation of parameters	0.001 * e.s.d
maximum peak height in diff. Fourier synthesis	0.36, -0.29 $eÅ^{-3}$

Final coordinates and equivalent displacement parameters (Å^2)

$U_{äq} = (1/3)*\sum\sum_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$

Atom	X	Y	Z	U_{eq}
C1	0.4299(2)	0.6121(2)	0.6548(2)	0.0321(8)
C2	0.4927(2)	0.5338(2)	0.6284(2)	0.0297(8)
N3	0.4433(2)	0.4125(1)	0.5710(1)	0.0315(7)
B4	0.3086(2)	0.3362(2)	0.5439(2)	0.0331(10)
N5	0.3067(2)	0.2065(2)	0.4755(1)	0.0348(7)
C6	0.1944(2)	0.1239(2)	0.4269(2)	0.044(1)
C7	0.1827(2)	0.0102(2)	0.3685(2)	0.050(1)
C8	0.2883(2)	-0.0238(2)	0.3567(2)	0.0440(10)
C9	0.4026(2)	0.0592(2)	0.4067(2)	0.0359(9)
C10	0.4120(2)	0.1782(2)	0.4673(2)	0.0321(8)
N11	0.5274(2)	0.2570(2)	0.5150(1)	0.0314(7)
C12	0.5384(2)	0.3680(2)	0.5641(2)	0.0300(8)
C13	0.6568(2)	0.4635(2)	0.6190(2)	0.0300(8)
C14	0.6264(2)	0.5655(2)	0.6590(2)	0.0305(8)
C15	0.6971(2)	0.6853(2)	0.7253(2)	0.0325(8)
C16	0.6337(2)	0.7629(2)	0.7530(2)	0.0312(8)
N17	0.6803(2)	0.8824(2)	0.8205(1)	0.0332(7)
B18	0.8092(2)	0.9506(2)	0.8845(2)	0.039(1)
N19	0.8087(2)	1.0794(2)	0.9501(1)	0.0350(7)
C20	0.9187(2)	1.1581(2)	1.0107(2)	0.0412(10)
C21	0.9278(2)	1.2696(2)	1.0756(2)	0.045(1)
C22	0.8225(2)	1.3034(2)	1.0803(2)	0.0419(10)
C23	0.7106(2)	1.2243(2)	1.0195(2)	0.0367(9)
C24	0.7033(2)	1.1087(2)	0.9502(2)	0.0334(8)
N25	0.5910(2)	1.0331(2)	0.8898(1)	0.0337(7)
C26	0.5839(2)	0.9254(2)	0.8302(2)	0.0323(8)
C27	0.4688(2)	0.8318(2)	0.7632(2)	0.0308(8)
F28	0.2677(1)	0.3368(1)	0.6286(1)	0.0430(6)
F29	0.2306(1)	0.3666(1)	0.4920(1)	0.0421(6)
O30	0.5128(2)	0.0411(1)	0.4050(1)	0.0402(7)
C31	0.5147(2)	-0.0730(2)	0.3374(2)	0.0399(9)
C32	0.6483(2)	-0.0663(2)	0.3447(2)	0.0381(9)
C33	0.6632(2)	-0.1740(2)	0.2619(2)	0.046(1)
C34	0.7963(2)	-0.1692(2)	0.2621(2)	0.045(1)
C35	0.8056(3)	-0.2723(3)	0.1719(3)	0.074(2)
C36	0.9344(3)	-0.2719(3)	0.1628(2)	0.066(1)
C37	0.7778(2)	0.4458(2)	0.6269(2)	0.0318(8)
C38	0.7865(2)	0.3372(2)	0.6161(2)	0.0361(9)
C39	0.9010(2)	0.3211(2)	0.6244(2)	0.0410(10)

C40	1.0089(2)	0.4118(2)	0.6454(2)	0.043(1)
C41	1.0009(2)	0.5188(2)	0.6544(2)	0.045(1)
C42	0.8878(2)	0.5355(2)	0.6447(2)	0.0376(9)
F43	0.8388(2)	0.9047(1)	0.9489(1)	0.0547(7)
F44	0.8986(1)	0.9567(1)	0.8293(1)	0.0576(7)
O45	0.6011(2)	1.2445(1)	1.0175(1)	0.0413(7)
C46	0.6013(2)	1.3595(2)	1.0840(2)	0.0389(9)
C47	0.4706(2)	1.3600(2)	1.0667(2)	0.0393(9)
C48	0.4612(2)	1.4827(2)	1.1232(2)	0.0388(9)
C49	0.3298(2)	1.4847(2)	1.1066(2)	0.043(1)
C50	0.3194(3)	1.6071(2)	1.1520(2)	0.045(1)
C51	0.1879(3)	1.6065(3)	1.1300(2)	0.058(1)
C52	0.3463(2)	0.8443(2)	0.7510(2)	0.0307(8)
C53	0.3096(2)	0.9219(2)	0.8302(2)	0.0355(9)
C54	0.1907(2)	0.9276(2)	0.8168(2)	0.0395(10)
C55	0.1063(2)	0.8573(2)	0.7260(2)	0.0392(10)
C56	0.1432(2)	0.7830(2)	0.6463(2)	0.0376(9)
C57	0.2618(2)	0.7771(2)	0.6584(2)	0.0327(8)
C58	0.5016(2)	0.7323(2)	0.7185(2)	0.0311(8)

Anisotropic displacement parameters

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	0.029(1)	0.033(1)	0.034(1)	0.0136(8)	0.0088(8)	0.0112(8)
C2	0.030(1)	0.0300(10)	0.0296(10)	0.0136(8)	0.0090(8)	0.0107(8)
N3	0.0291(9)	0.0299(9)	0.0353(9)	0.0137(7)	0.0098(7)	0.0111(7)
B4	0.031(1)	0.036(1)	0.036(1)	0.0152(10)	0.0113(10)	0.016(1)
N5	0.0306(9)	0.0346(9)	0.0383(10)	0.0117(7)	0.0078(8)	0.0147(8)
C6	0.029(1)	0.040(1)	0.054(1)	0.0109(9)	0.005(1)	0.014(1)
C7	0.035(1)	0.043(1)	0.056(2)	0.007(1)	0.001(1)	0.012(1)
C8	0.038(1)	0.036(1)	0.047(1)	0.0106(10)	0.008(1)	0.010(1)
C9	0.037(1)	0.035(1)	0.037(1)	0.0147(9)	0.0110(9)	0.0133(9)
C10	0.030(1)	0.032(1)	0.034(1)	0.0109(8)	0.0087(8)	0.0134(9)
N11	0.0304(9)	0.0293(8)	0.0344(9)	0.0123(7)	0.0111(7)	0.0116(7)
C12	0.0284(10)	0.034(1)	0.032(1)	0.0154(8)	0.0115(8)	0.0147(8)
C13	0.029(1)	0.0318(10)	0.031(1)	0.0127(8)	0.0097(8)	0.0126(8)
C14	0.0280(10)	0.033(1)	0.033(1)	0.0151(8)	0.0104(8)	0.0133(8)
C15	0.029(1)	0.034(1)	0.034(1)	0.0150(8)	0.0092(8)	0.0117(9)
C16	0.031(1)	0.0299(10)	0.030(1)	0.0119(8)	0.0070(8)	0.0094(8)
N17	0.0326(9)	0.0300(9)	0.0333(9)	0.0145(7)	0.0068(7)	0.0078(7)

B18	0.032(1)	0.040(1)	0.040(1)	0.019(1)	0.007(1)	0.008(1)
N19	0.0328(9)	0.0354(9)	0.0357(10)	0.0141(8)	0.0073(8)	0.0130(8)
C20	0.032(1)	0.042(1)	0.044(1)	0.0138(10)	0.0043(10)	0.012(1)
C21	0.036(1)	0.040(1)	0.046(1)	0.0109(10)	0.001(1)	0.010(1)
C22	0.043(1)	0.035(1)	0.040(1)	0.0157(10)	0.005(1)	0.0079(10)
C23	0.035(1)	0.036(1)	0.038(1)	0.0178(9)	0.0083(9)	0.0124(9)
C24	0.031(1)	0.032(1)	0.036(1)	0.0140(8)	0.0070(9)	0.0116(9)
N25	0.0322(9)	0.0322(9)	0.0349(9)	0.0152(7)	0.0069(7)	0.0104(7)
C26	0.032(1)	0.034(1)	0.032(1)	0.0168(9)	0.0091(8)	0.0125(9)
C27	0.032(1)	0.0322(10)	0.0303(10)	0.0137(8)	0.0095(8)	0.0129(8)
F28	0.0424(8)	0.0473(7)	0.0463(8)	0.0185(6)	0.0236(6)	0.0222(6)
F29	0.0325(7)	0.0435(7)	0.0549(8)	0.0180(6)	0.0075(6)	0.0231(6)
O30	0.0351(8)	0.0301(7)	0.0482(9)	0.0131(6)	0.0128(7)	0.0082(7)
C31	0.046(1)	0.026(1)	0.043(1)	0.0151(9)	0.012(1)	0.0085(9)
C32	0.041(1)	0.033(1)	0.040(1)	0.0161(9)	0.0121(10)	0.0133(9)
C33	0.047(1)	0.042(1)	0.046(1)	0.024(1)	0.012(1)	0.011(1)
C34	0.046(1)	0.042(1)	0.052(1)	0.022(1)	0.019(1)	0.019(1)
C35	0.057(2)	0.072(2)	0.065(2)	0.035(2)	0.008(1)	-0.005(2)
C36	0.056(2)	0.079(2)	0.053(2)	0.035(2)	0.014(1)	0.011(1)
C37	0.031(1)	0.033(1)	0.031(1)	0.0151(8)	0.0092(8)	0.0104(8)
C38	0.034(1)	0.034(1)	0.040(1)	0.0151(9)	0.0099(9)	0.0137(9)
C39	0.038(1)	0.041(1)	0.046(1)	0.021(1)	0.011(1)	0.016(1)
C40	0.034(1)	0.054(1)	0.050(1)	0.025(1)	0.014(1)	0.023(1)
C41	0.030(1)	0.047(1)	0.063(2)	0.015(1)	0.014(1)	0.026(1)
C42	0.031(1)	0.036(1)	0.046(1)	0.0135(9)	0.0104(9)	0.0167(10)
F43	0.0577(9)	0.0442(8)	0.0540(9)	0.0259(7)	-0.0077(7)	0.0123(7)
F44	0.0350(8)	0.0560(9)	0.0573(9)	0.0145(7)	0.0179(7)	0.0001(7)
O45	0.0373(9)	0.0319(8)	0.0462(9)	0.0164(7)	0.0083(7)	0.0060(7)
C46	0.044(1)	0.032(1)	0.037(1)	0.0176(10)	0.0109(10)	0.0090(9)
C47	0.040(1)	0.034(1)	0.041(1)	0.0164(9)	0.0113(10)	0.0116(9)
C48	0.042(1)	0.034(1)	0.039(1)	0.0177(10)	0.0123(10)	0.0119(9)
C49	0.043(1)	0.042(1)	0.042(1)	0.020(1)	0.010(1)	0.013(1)
C50	0.051(1)	0.043(1)	0.046(1)	0.026(1)	0.019(1)	0.015(1)
C51	0.061(2)	0.064(2)	0.058(2)	0.040(1)	0.019(1)	0.021(1)
C52	0.030(1)	0.0304(10)	0.035(1)	0.0140(8)	0.0119(8)	0.0145(8)
C53	0.038(1)	0.038(1)	0.034(1)	0.0195(9)	0.0134(9)	0.0138(9)
C54	0.040(1)	0.043(1)	0.046(1)	0.024(1)	0.022(1)	0.021(1)
C55	0.032(1)	0.048(1)	0.048(1)	0.0192(10)	0.0166(10)	0.025(1)
C56	0.033(1)	0.040(1)	0.041(1)	0.0146(9)	0.0085(9)	0.0170(10)
C57	0.033(1)	0.032(1)	0.035(1)	0.0139(8)	0.0105(9)	0.0134(9)
C58	0.030(1)	0.035(1)	0.033(1)	0.0164(9)	0.0114(8)	0.0159(9)

Final coordinates and isotropic displacement parameters (Å^2) for H- atoms

Atom	X	Y	Z	U_{iso}
H1	0.34266	0.58819	0.63204	0.0385
H6	0.12194	0.14591	0.43386	0.052
H7	0.10268	-0.04643	0.33562	0.060
H8	0.28095	-0.10280	0.31480	0.053
H15	0.78420	0.70941	0.74885	0.0390
H20	0.99076	1.13522	1.00799	0.049
H21	1.00570	1.32385	1.11739	0.054
H22	0.82793	1.38077	1.12533	0.050
H31A	0.47488	-0.09370	0.26806	0.048
H31B	0.46927	-0.13367	0.35643	0.048
H32A	0.68254	-0.06015	0.41062	0.046
H32B	0.69616	0.00524	0.34011	0.046
H33A	0.61839	-0.24471	0.26904	0.056
H33B	0.62397	-0.18241	0.19644	0.056
H34A	0.83356	-0.16997	0.32409	0.054
H34B	0.84385	-0.09487	0.26155	0.054
H35A	0.76044	-0.34579	0.17483	0.089
H35B	0.76314	-0.27350	0.11065	0.089
H36A	0.93100	-0.34201	0.10329	0.099
H36B	0.97741	-0.27220	0.22245	0.099
H36C	0.97936	-0.20138	0.15675	0.099
H38	0.71335	0.27427	0.60294	0.043
H39	0.90535	0.24653	0.61547	0.049
H40	1.08730	0.40103	0.65349	0.052
H41	1.07441	0.58128	0.66755	0.054
H42	0.88422	0.60908	0.65012	0.045
H46A	0.65682	1.41999	1.06970	0.047
H46B	0.63085	1.37650	1.15439	0.047
H47A	0.41828	1.30561	1.08872	0.047
H47B	0.43823	1.33099	0.99423	0.047
H48A	0.49381	1.51154	1.19570	0.047
H48B	0.51376	1.53692	1.10126	0.047
H49A	0.27977	1.43754	1.13572	0.051
H49B	0.29404	1.44678	1.03376	0.051
H50A	0.35108	1.64389	1.22535	0.054
H50B	0.37215	1.65567	1.12525	0.054
H51A	0.15517	1.56837	1.05745	0.088
H51B	0.18676	1.68755	1.15796	0.088
H51C	0.13634	1.56331	1.16040	0.088
H53	0.36633	0.97052	0.89296	0.043

H54	0.16674	0.98044	0.87081	0.047
H55	0.02407	0.85988	0.71829	0.047
H56	0.08660	0.73606	0.58322	0.045
H57	0.28636	0.72677	0.60314	0.0392

Crystal data for *aza*-BODIPY 9

formula	$C_{44}H_{42}B_2F_6N_6O_2$, $2(CH_2Cl_2)$
molecular weight	992.31 $gmol^{-1}$
absorption	μ = 2.908 mm^{-1}
crystal size	0.08 x 0.25 x 0.6 mm^3 black needle
space group	P 2_1/c (monoclinic)
lattice parameters	a = 4.7273(4)Å
(calculate from	b = 19.7110(10)Å ß = 97.316(7)°
27380 reflections with	c = 25.181(2)Å
1.8° < θ < 66.6°)	V=2327.2(3)$Å^3$ z = 2 F(000) = 1024
temperature	-80°C
density	d_{xray} = 1.416 gcm^{-3}

data collection

diffractometer	STOE IPDS 2T
radiation	Mo-K_α Graphitmonochromator
Scan – type	ω scans
Scan – width	1°
scan range	2° ≤ θ < 68°
	-5 ≤ h ≤ 5 -23 ≤ k ≤ 23 -29 ≤ l ≤ 30
number of reflections:	
measured	29890
unique	4141 (R_{int} = 0.2707)
observed	1828 (|F|/σ(F) > 4.0)

daten correction, structure solution and refinement

corrections	Lorentz and polarisation correction.
Structure solution	Program: SIR-97 (Direct methods)
refinement	Program: SHELXL-97 (full matrix). 337 refined parameters, weighting scheme: $w=1/[\sigma^2(F_o^2) + (0.2*P)^2]$ with $(Max(F_o^2,0)+2*F_c^2)/3$. H-atoms at calculated positions and refined with isotropic displacement parameters, non H- atoms refined anisotropically.
R-values	wR2 = 0.479 (R1 = 0.1847 for observed reflections, 0.2451 for all reflections)
goodness of fit	S = 1.445
maximum deviation of parameters	0.001 * e.s.d
maximum peak height in diff. Fourier synthesis	0.62, -0.57 e$Å^{-3}$
remark	molecule has C_i symmetry

Final coordinates and equivalent displacement parameters (Å^2)

$U_{äq} = (1/3)*\sum\sum_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$

Atom	X	Y	Z	U_{eq}
N1	-0.060(2)	0.6607(4)	0.5721(3)	0.072(3)
C2	0.092(2)	0.6155(5)	0.5509(3)	0.065(3)
C3	0.115(2)	0.6071(5)	0.4932(4)	0.074(4)
C4	0.303(2)	0.5535(5)	0.4896(3)	0.066(3)
C5	0.403(2)	0.5301(5)	0.5431(4)	0.064(3)
N6	0.270(2)	0.5695(4)	0.5798(3)	0.072(3)
B7	0.300(2)	0.5631(6)	0.6406(5)	0.068(4)
N8	0.137(2)	0.6267(4)	0.6599(3)	0.071(3)
C8	0.591(2)	0.4792(5)	0.5547(4)	0.072(3)
C9	0.156(2)	0.6350(6)	0.7156(4)	0.080(4)
C10	0.003(2)	0.6838(5)	0.7366(4)	0.080(4)
C11	-0.189(2)	0.7236(6)	0.7028(4)	0.081(4)
C12	-0.205(2)	0.7163(5)	0.6494(4)	0.071(3)
C13	-0.043(2)	0.6653(5)	0.6271(3)	0.068(3)
C14	-0.032(2)	0.6501(5)	0.4518(4)	0.073(4)
C17	-0.303(3)	0.7339(7)	0.3714(5)	0.098(5)
C15A	-0.12(1)	0.717(1)	0.464(1)	0.10(1)
C16A	-0.242(8)	0.760(2)	0.421(1)	0.10(1)
C19A	-0.213(7)	0.669(1)	0.359(1)	0.078(10)
C20A	-0.095(6)	0.627(1)	0.3995(9)	0.071(8)
C15B	-0.284(6)	0.687(2)	0.4590(10)	0.079(9)
C16B	-0.404(8)	0.731(1)	0.420(1)	0.09(1)
C18B	-0.09(1)	0.701(2)	0.362(1)	0.13(2)
C19B	0.070(9)	0.657(2)	0.4028(9)	0.10(1)
F20	-0.429(2)	0.7739(5)	0.3319(3)	0.127(4)
F21	0.176(1)	0.5041(3)	0.6573(2)	0.080(2)
F22	0.582(1)	0.5651(3)	0.6636(2)	0.079(2)
O23	-0.385(2)	0.7512(3)	0.6117(3)	0.077(2)
C24	-0.546(2)	0.8061(5)	0.6318(5)	0.083(4)
C25	-0.741(3)	0.8335(6)	0.5844(5)	0.100(5)
C26	-0.579(3)	0.8656(7)	0.5413(6)	0.111(6)
C27	-0.796(3)	0.8904(8)	0.4928(6)	0.124(7)
C28	-0.657(3)	0.9212(9)	0.4489(7)	0.135(7)
C29	-0.870(5)	0.943(2)	0.4015(8)	0.21(1)
C1L	0.254(5)	0.953(1)	0.7546(8)	0.18(1)
CL2L	0.165(2)	0.8719(3)	0.7441(3)	0.220(4)
CL3L	0.403(2)	0.9898(3)	0.7043(2)	0.182(3)

Anisotropic displacement parameters

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N1	0.079(6)	0.078(5)	0.061(4)	0.004(4)	0.017(4)	-0.006(3)
C2	0.062(6)	0.076(5)	0.056(4)	-0.001(4)	0.003(4)	0.003(4)
C3	0.087(7)	0.078(6)	0.061(5)	0.010(5)	0.020(5)	0.000(4)
C4	0.064(6)	0.074(5)	0.063(5)	-0.001(4)	0.014(4)	0.000(4)
C5	0.056(6)	0.073(5)	0.065(5)	0.002(4)	0.012(4)	-0.001(4)
N6	0.081(6)	0.076(4)	0.062(4)	0.012(4)	0.022(4)	0.002(3)
B7	0.050(7)	0.074(6)	0.077(6)	0.001(5)	0.000(5)	0.002(5)
N8	0.071(5)	0.087(5)	0.057(4)	-0.003(4)	0.014(4)	-0.002(4)
C8	0.081(7)	0.080(6)	0.058(4)	0.004(5)	0.021(5)	0.005(4)
C9	0.085(8)	0.101(7)	0.052(5)	-0.008(6)	0.003(5)	-0.006(4)
C10	0.084(7)	0.092(7)	0.066(5)	0.007(6)	0.018(5)	-0.015(5)
C11	0.083(8)	0.091(6)	0.069(6)	0.013(6)	0.009(5)	-0.005(5)
C12	0.067(6)	0.079(5)	0.069(5)	-0.001(5)	0.016(5)	-0.005(4)
C13	0.066(6)	0.082(6)	0.056(5)	0.005(5)	0.011(4)	-0.002(4)
C14	0.077(7)	0.081(6)	0.061(5)	0.003(5)	0.004(5)	-0.014(4)
C17	0.12(1)	0.098(8)	0.075(7)	0.020(8)	0.020(7)	0.022(6)
C15A	0.16(4)	0.07(2)	0.07(1)	0.03(2)	-0.02(2)	-0.01(1)
C16A	0.10(2)	0.09(2)	0.10(2)	0.00(2)	-0.03(2)	-0.01(2)
C19A	0.09(2)	0.07(2)	0.07(1)	0.01(1)	0.02(1)	0.01(1)
C20A	0.06(2)	0.09(1)	0.07(1)	-0.01(1)	0.01(1)	-0.01(1)
C15B	0.06(2)	0.10(2)	0.07(1)	0.01(1)	0.02(1)	0.01(1)
C16B	0.11(2)	0.08(2)	0.08(1)	0.02(2)	0.03(2)	0.01(1)
C18B	0.20(5)	0.13(3)	0.08(2)	0.05(3)	0.07(2)	0.04(2)
C19B	0.12(3)	0.11(2)	0.06(1)	0.05(2)	0.04(2)	0.02(1)
F20	0.143(7)	0.146(6)	0.089(4)	0.041(5)	0.006(4)	0.032(4)
F21	0.095(4)	0.075(3)	0.074(3)	-0.002(3)	0.024(3)	0.010(2)
F22	0.074(4)	0.096(4)	0.068(3)	0.003(3)	0.014(3)	-0.001(3)
O23	0.078(5)	0.082(4)	0.073(4)	0.015(3)	0.019(3)	-0.002(3)
C24	0.075(7)	0.081(6)	0.093(7)	0.013(5)	0.011(6)	-0.002(5)
C25	0.107(10)	0.090(7)	0.107(8)	0.009(7)	0.033(8)	0.007(6)
C26	0.12(1)	0.100(8)	0.117(9)	0.018(8)	0.044(9)	0.034(7)
C27	0.11(1)	0.14(1)	0.12(1)	0.010(9)	0.012(9)	0.047(9)
C28	0.10(1)	0.17(1)	0.14(1)	0.000(10)	0.018(9)	0.05(1)
C29	0.17(2)	0.34(3)	0.14(2)	0.01(2)	0.04(1)	0.14(2)
C1L	0.19(2)	0.20(2)	0.18(2)	-0.08(2)	0.12(2)	-0.08(1)
CL2L	0.297(8)	0.203(5)	0.190(5)	-0.123(6)	0.145(6)	-0.093(4)
CL3L	0.256(7)	0.180(5)	0.113(3)	-0.055(5)	0.032(4)	-0.008(3)

Final coordinates and isotropic displacement parameters (Å^2) for H- atoms

Atom	X	Y	Z	U_{iso}
H8	0.65116	0.46576	0.59059	0.086
H9	0.27617	0.60611	0.73868	0.096
H10	0.02612	0.69117	0.77416	0.096
H11	-0.30692	0.75560	0.71766	0.098
H15A	-0.09956	0.73286	0.50022	0.12
H16A	-0.27928	0.80647	0.42752	0.12
H19A	-0.23341	0.65344	0.32316	0.09
H20A	-0.05548	0.58140	0.39147	0.086
H15B	-0.36998	0.68024	0.49075	0.09
H16B	-0.55657	0.75944	0.42735	0.11
H18B	-0.02289	0.70502	0.32795	0.16
H19B	0.23790	0.63440	0.39582	0.12
H24A	-0.41542	0.84205	0.64772	0.099
H24B	-0.65857	0.78911	0.65955	0.099
H25A	-0.86810	0.86799	0.59723	0.120
H25B	-0.86131	0.79607	0.56803	0.120
H26A	-0.44709	0.83186	0.52880	0.133
H26B	-0.46423	0.90453	0.55683	0.133
H27A	-0.91264	0.85131	0.47842	0.149
H27B	-0.92548	0.92419	0.50588	0.149
H28A	-0.52309	0.88786	0.43643	0.162
H28B	-0.54468	0.96113	0.46294	0.162
H29A	-0.96779	0.90302	0.38503	0.32
H29B	-0.76892	0.96629	0.37513	0.32
H29C	-1.01011	0.97395	0.41393	0.32
H1L1	0.38891	0.95591	0.78790	0.22
H1L2	0.08025	0.97851	0.76030	0.22