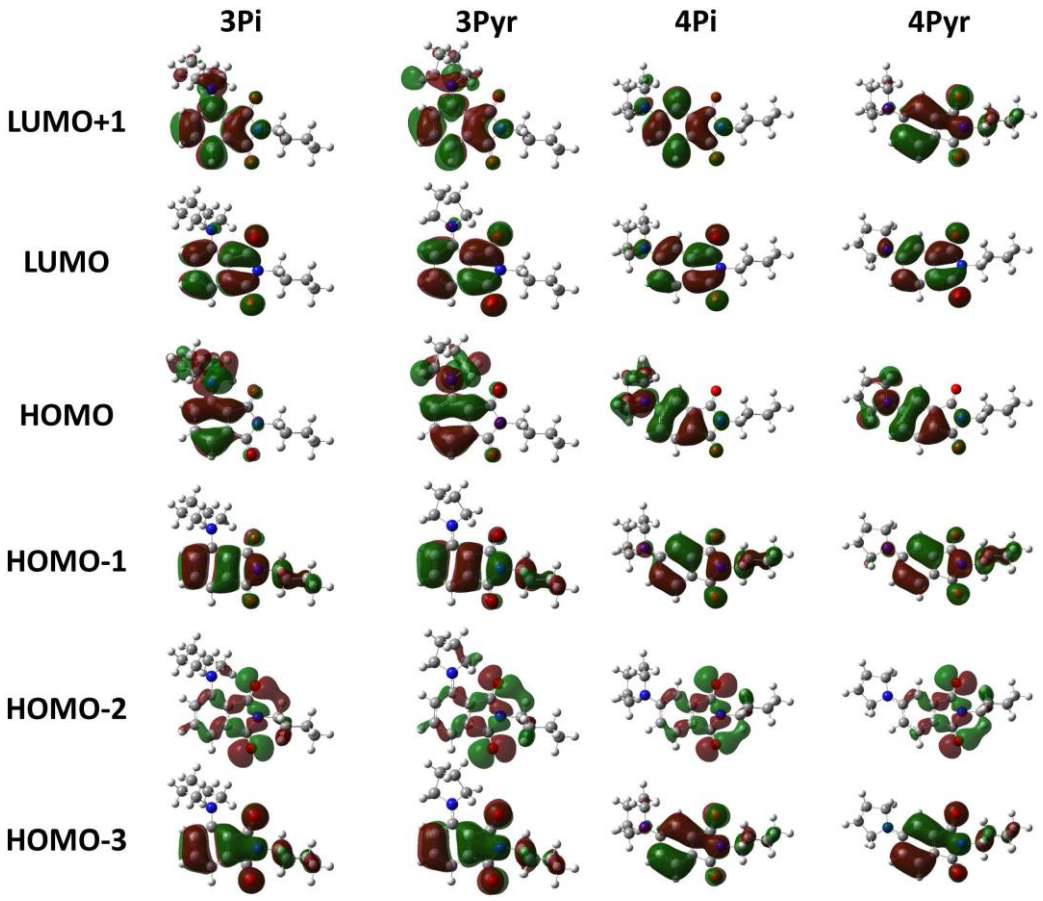
Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information (ESI)

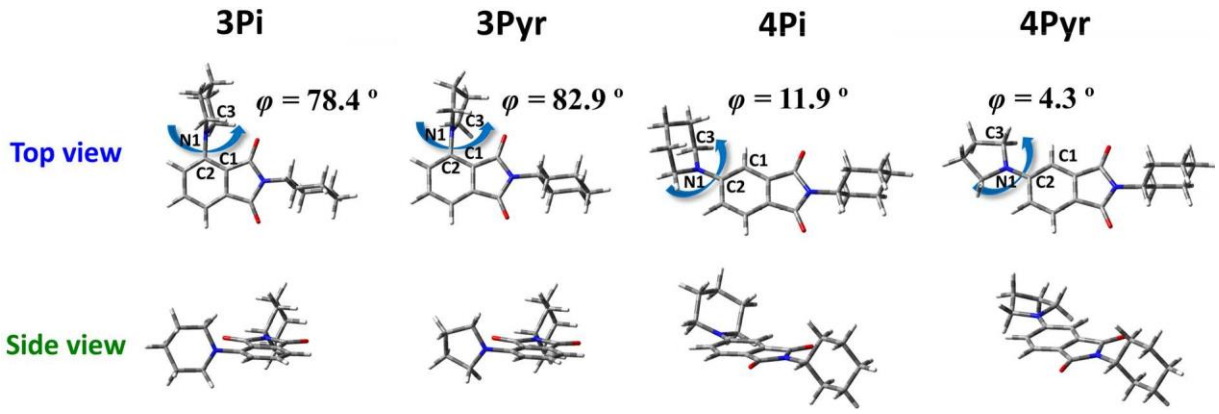
Enhanced Fluorescence of Phthalimide Compounds Induced by the Incorporation of Electron-Donating Alicyclic Amino Groups

Ryoji Orita[†], Marius Franckevičius[‡], Aurimas Vyšniauskas[‡], Vidmantas Gulbinas[‡], Haruki Sugiyama[§], Hidehiro Uekusa[§], Kenta Kanosue[†], Ryohei Ishige[†], and Shinji Ando*[†]

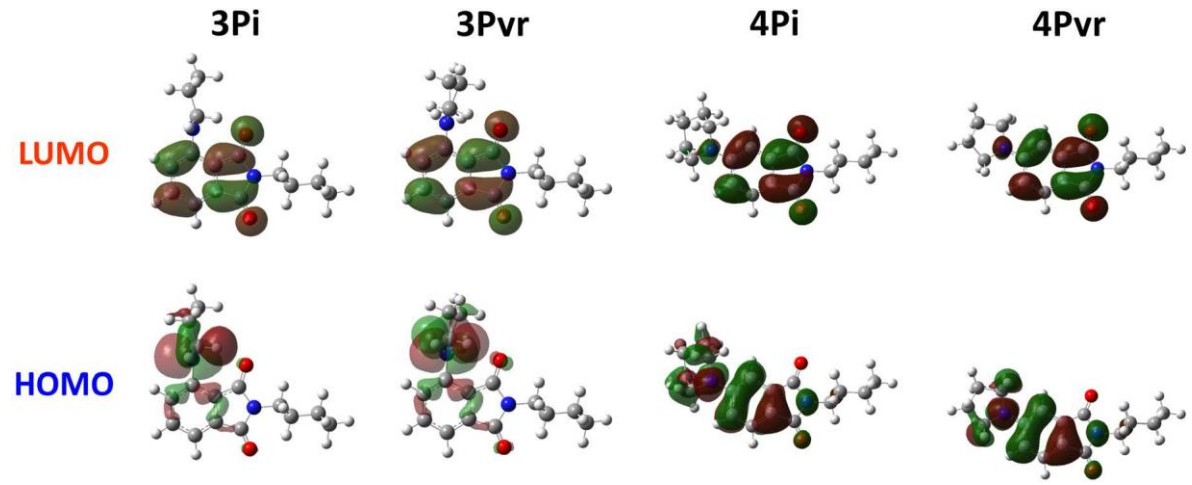
a. [†]Department of Chemical Science and Engineering, Tokyo Institute of Technology, Ookayama 2-12-1-E4-5, Meguro-ku, Tokyo 152-8552, Japan
b. [‡]Center for Physical Sciences and Technology, Saulėtekio Av. 3, Vilnius LT-10257, Lithuania
c. [§]Department of Chemistry, Tokyo Institute of Technology, Ookayama 2-12-1-H62, Meguro-ku, Tokyo 152-8552, Japan



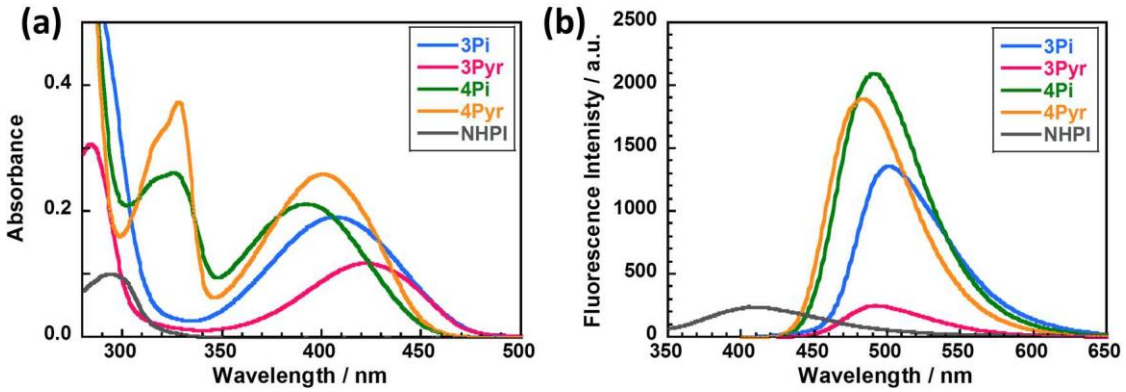
FigureS1 Calculated molecular orbitals of **x-NHPI**s in the ground S_0 state (TD-DFT method at the CAM-B3LYP/6-311+G(d,p) level).



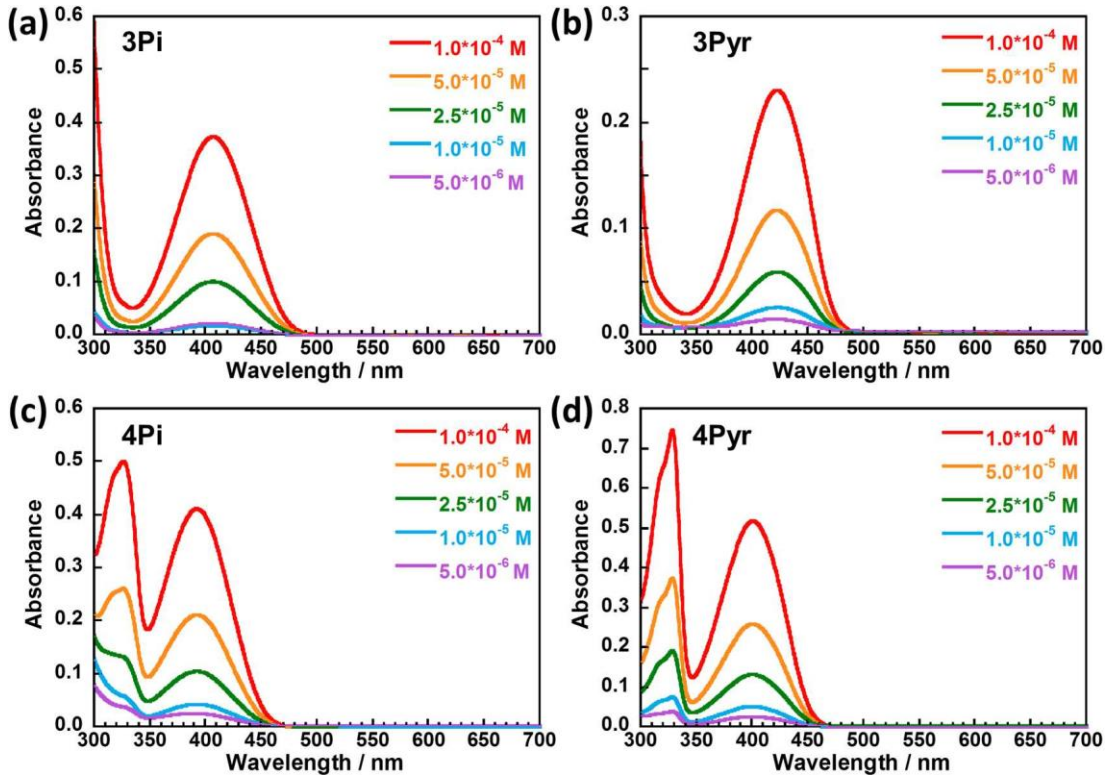
FigureS2 Calculated optimized geometry (top and side view) of **x-NHPI**s in the S_1 state and the atom labelling convention of **x-NHPI**s. The dihedral angles (φ) of alicyclic amino group and phthalimide moiety for **x-NHPI**s are defined by C1-C2-N1-C3.



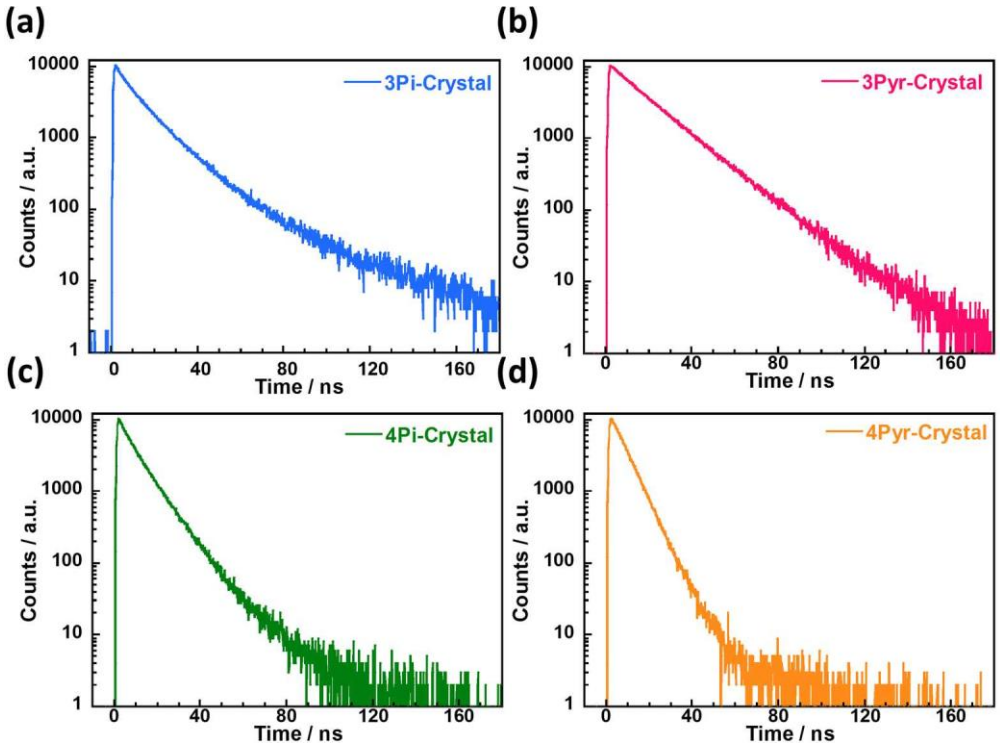
FigureS3 Calculated molecular orbitals of **x-NHPI**s in the excited S_1 state (TD-DFT method at the CAM-B3LYP/6-311+G(d,p) level).



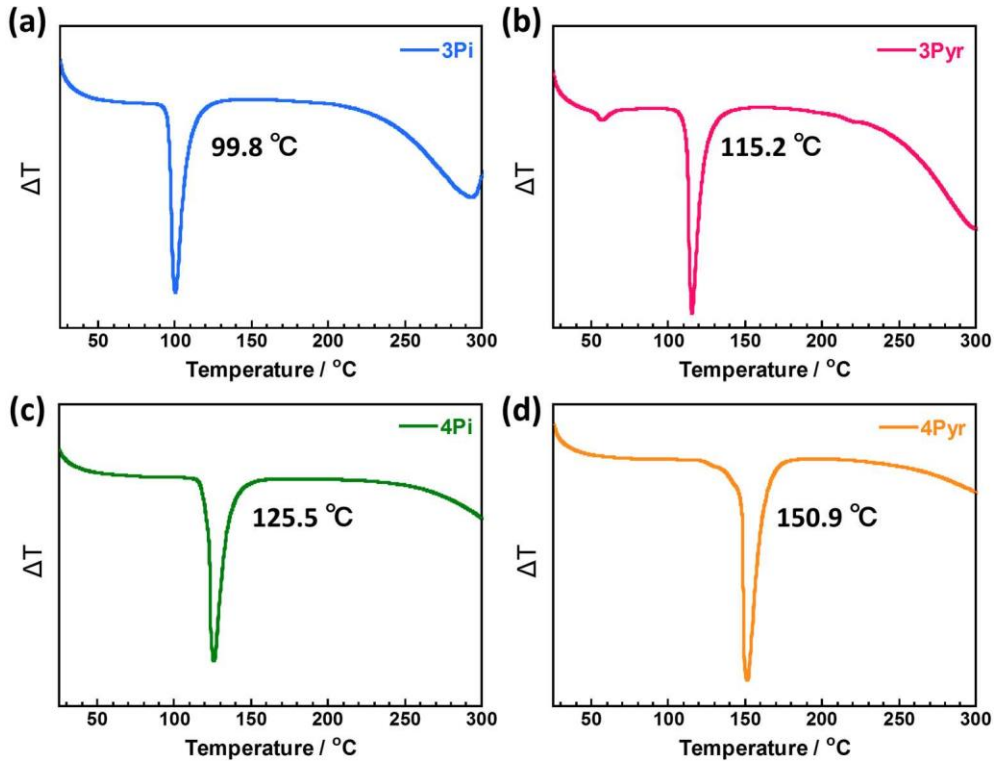
FigureS4 (a) UV/Vis absorption spectra and (b) fluorescence spectra of **NHPI** and **x-NHPI**s in $CHCl_3$ (5.0×10^{-5} M). Excitation wavelengths for NHPI is 295 nm, and for **x-NHPI**s are listed in Table 1. The fluorescence intensities of 3Pi and 3Pyr are 10 times and that of NHPI is 100 times.



FigureS5 UV/Vis absorption spectra of (a) **3Pi**, (b) **3Pyr**, (c) **4Pi**, and (d) **4Pyr** in $CHCl_3$ at different concentrations (5.0×10^{-6}–1.0×10^{-4} M).



FigureS6 Fluorescence decay profiles of (a) **3Pi**, (b) **3Pyr**, (c) **4Pi**, (d) **4Pyr** in crystalline state. The wavelength for excitation were set to 365 nm. The observed emission wavelengths (λ_{em}) are 565 nm for **3Pi**, 550 nm for **3Pyr**, 490 nm for **4Pi**, 510 nm for **4Pyr**



FigureS7 DTA curves of crystalline samples of (a) **3Pi**, (b) **3Pyr**, (c) **4Pi**, (d) **4Pyr**. Melting point (°C) of each compound is shown in the figure.

Table S1 Calculated electronic transitions of **x-NHPI**s in optimized S_1 geometry.

Compound	State	Transition wavelength (nm)	Oscillator strength	Orbitals			Assignment
3Pi	S_1	775.3	0.0000	HOMO	→	LUMO	CT(π–π^*)
3Pyr	S_1	796.1	0.0000	HOMO	→	LUMO	CT(π–π^*)
4Pi	S_1	458.5	0.0630	HOMO	→	LUMO	HLCT(π–π^*)
4Pyr	S_1	445.2	0.0595	HOMO	→	LUMO	HLCT(π–π^*)

Table S2 Ground and excited state dipole moments for **x-NHPI**s.

Compound	Slope[a]	a_0[b] (A)	$\mu_{g(cal)}$[c] (D)	$\mu_{e(exp)}$[d] (D)
3Pi	7387	4.66	3.62	12.6
3Pyr	5816	4.50	4.06	11.3
4Pi	7494	4.59	4.87	13.4
4Pyr	7430	4.51	5.64	13.9

[a] The slopes of the linear relations in Figure 4, [b] the dipole moment in S_0 state calculated by DFT calculations, [c] the Onsagar cavity radius obtained from Eq. (5), [d] the dipole moment in S_1 state obtained from Eqs. (1) and (3).

Table S3 Crystal data and structure refinement of **3Pi**.

Empirical formula	$C_{19}H_{24}N_2O_2$	
Formula weight	312.4	
Temperature	173(2) K	
Wavelength	1.54186 Å	
Crystal system	Monoclinic	
Space group	$P\ 2_1/n$	
Unit cell dimensions	a = 6.7785(2) Å	
	b = 9.8025(3) Å	β= 94.7017(18)°.
	c = 25.4462(7) Å	
Volume	1685.11(9) $Å^3$	
Z	4	
Density (calculated)	1.231 g/cm^3	
Absorption coefficient	0.636 mm^{-1}	
F(000)	672	
Crystal size	0.239 x 0.197 x 0.106 mm^3	
Theta range for data collection	3.486 to 68.253°.	
Index ranges	-8<=h<=8, -11<=k<=11, -30<=l<=30	
Reflections collected	29533	
Independent reflections	3080 [R(int) = 0.0422]	
Completeness to theta = 67.686°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.936 and 0.815	
Refinement method	Full-matrix least-squares on F_2	
Data / restraints / parameters	3075 / 0 / 208	
Goodness-of-fit on F_2	1.125	
Final R indices [I>2sigma(I)]	R_1 = 0.0357, wR_2 = 0.0971	
R indices (all data)	R_1 = 0.0404, wR_2 = 0.1001	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.190 and -0.206 e.$Å^{-3}$	
CCDC number	1815929	

Table S4 Crystal data and structure refinement of **3Pyr**.

Empirical formula	$C_{18}H_{22}N_2O_2$	
Formula weight	298.37	
Temperature	173(2) K	
Wavelength	1.54186 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 10.7455(9) Å	
	b = 26.6113(17) Å	= 99.080(4)°.
	c = 10.8489(7) Å	
Volume	3063.4(4) $Å^3$	
Z	8	
Density (calculated)	1.294 g/cm^3	
Absorption coefficient	0.675 mm^{-1}	
F(000)	1280	
Crystal size	0.338 x 0.099 x 0.098 mm^3	
Theta range for data collection	4.166 to 68.247°.	
Index ranges	-12<=h<=12, -32<=k<=32, -13<=l<=12	
Reflections collected	34608	
Independent reflections	5591 [R(int) = 0.1072]	
Completeness to theta = 67.686°	100.00 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.937 and 0.664	
Refinement method	Full-matrix least-squares on F_2	
Data / restraints / parameters	5591 / 0 / 397	
Goodness-of-fit on F_2	0.833	
Final R indices [I>2sigma(I)]	R_1 = 0.0489, wR_2 = 0.0944	
R indices (all data)	R_1 = 0.0917, wR_2 = 0.1187	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.241 and -0.232 e.$Å^{-3}$	
CCDC number	1815930	

Table S5 Crystal data and structure refinement of **4Pi**.

Empirical formula	$C_{19}H_{24}N_2O_2$	
Formula weight	312.4	
Temperature	173(2) K	
Wavelength	1.54186 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 5.26649(14) Å	α= 72.6185(17)°.
	b = 10.6373(3) Å	= 89.9112(17)°.
	c = 15.2944(5) Å	γ = 83.0728(16)°.
Volume	811.18(4) Å^3	
Z	2	
Density (calculated)	1.279 g/cm^3	
Absorption coefficient	0.660 mm^{-1}	
F(000)	336	
Crystal size	0.324 x 0.058 x 0.055 mm^3	
Theta range for data collection	3.030 to 68.139°.	
Index ranges	-6<=h<=6, -12<=k<=12, -18<=l<=18	
Reflections collected	9616	
Independent reflections	2924 [R(int) = 0.0671]	
Completeness to theta = 67.686°	98.40 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.965 and 0.736	
Refinement method	Full-matrix least-squares on F_2	
Data / restraints / parameters	2924 / 0 / 304	
Goodness-of-fit on F_2	0.968	
Final R indices [I>2sigma(I)]	R_1 = 0.0530, wR_2 = 0.1298	
R indices (all data)	R_1 = 0.0677, wR_2 = 0.1497	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.253 and -0.234 e.Å^{-3}	
CCDC number	1815931	

Table S6 Crystal data and structure refinement of **4Pyr**.

Empirical formula	$C_{18}H_{22}N_2O_2$	
Formula weight	298.37	
Temperature	173(2) K	
Wavelength	1.54186 Å	
Crystal system	Monoclinic	
Space group	*P* $2_1/c$	
Unit cell dimensions	*a* = 5.1353(2) Å	
	b = 10.3387(4) Å	β= 92.523(3)°.
	c = 29.0552(12) Å	
Volume	1541.11(10) $Å^3$	
Z	4	
Density (calculated)	1.286 g/cm^3	
Absorption coefficient	0.671 mm^{-1}	
F(000)	640	
Crystal size	0.271 x 0.106 x 0.100 mm^3	
Theta range for data collection	3.045 to 68.220°.	
Index ranges	-6<=*h*<=6, -12<=*k*<=12, -34<=*l*<=34	
Reflections collected	17004	
Independent reflections	2818 [*R*(int) = 0.0540]	
Completeness to theta = 67.686°	100.00 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.936 and 0.0481104	
Refinement method	Full-matrix least-squares on F_2	
Data / restraints / parameters	2818 / 0 / 287	
Goodness-of-fit on F_2	0.961	
Final *R* indices [*I*>2sigma(*I*)]	R_1 = 0.0396, wR_2 = 0.0862	
R indices (all data)	R_1 = 0.0504, wR_2 = 0.0906	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.233 and -0.161 e.$Å^{-3}$	
CCDC number	1815932	