ESI for the article: Dynamic Single Crystal to Polycrystal Transformation of a 1D-Coordination Polymer and its Second Harmonic Generation.

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and it becomes amorphous after that. The thermal stability of **1** is quite good for a 1D coordination polymer. Synchrotron radiation: Wavelength: 0.61996808Å.

Figure S11. (a) XRPD pattern obtained after instant synthesis of **L** and $ZnBr_2$ in $CHCl_3$; (b) experimental XRPD pattern of **1** obtained after the instant synthesis of **L** and ZnI_2.

Figure S12. (a) XRPD pattern obtained after instant synthesis of **L** and $ZnBr_2$ in $CHCl_3$; experimental XRPD pattern of **1** obtained after the instant synthesis of **L** and $ZnCl_2$ (a).

SHG Experiments Set Up

Experimental Mehotds

All reagents were used as purchased, without further purification.

The ^{1}H NMR and ^{13}C NMR experiments were carried out using a Bruker Avance 400 MHz instrument.

The IR experiments were carried out using a Varian 640 equipped with a ATR module.

Then Elemental Analyses experiments were carried out using a Costech ECS mod. 4010.

ESI-MS data was measured using a Esquire 3000+ spectrometer working in continuous flow electrospray ionization method.

Single crystal X-ray diffraction experiments were carried out using a Bruker X8 Prospector diffractometer.

The powder X-ray diffraction data of **1** was recorded at ambient temperature in transmission mode on a Bruker D8 diffractometer.

1. Synthesis of ligand L.

L was synthesized by adding 160 mg of 4-(4-formyl-phenyl) pyridine (0.87 mmol) and 50 mg of 1,4 diaminocyclohexane (0.44 mmol) in 10 mL of MeCN (Figure S1). The solution was maintained under refluxing conditions for 4h and then left under stirring at r.t. overnight. The product, in the form of a white precipitate, is filtered off and washed with diethylether. Yield = 85%.

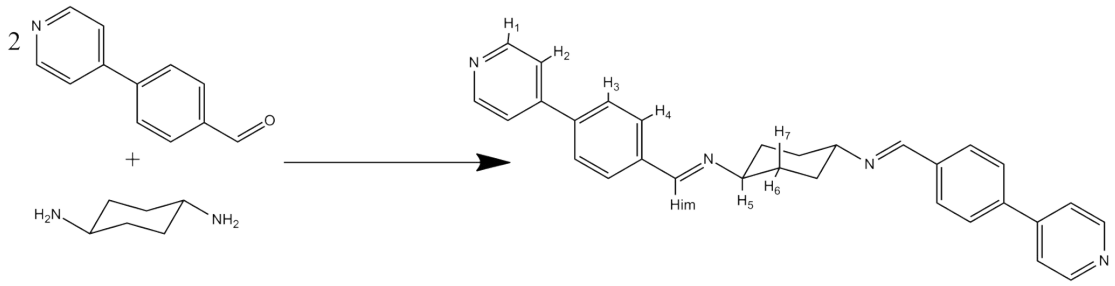

Figure S1. Scheme of the synthesis of **L**.

^{1}H-NMR and ^{13}C-NMR Characterization of L

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (dd, *J* = 4.5, 1.6 Hz, 4H), 8.44 (s, 2H), 7.87 (d, *J* = 8.3 Hz, 4H), 7.70 (d, *J* = 8.3 Hz, 4H), 7.54 (dd, *J* = 4.5, 1.6 Hz, 4H), 3.34 (s, broad, 2H), 1.89 (m, 8H)

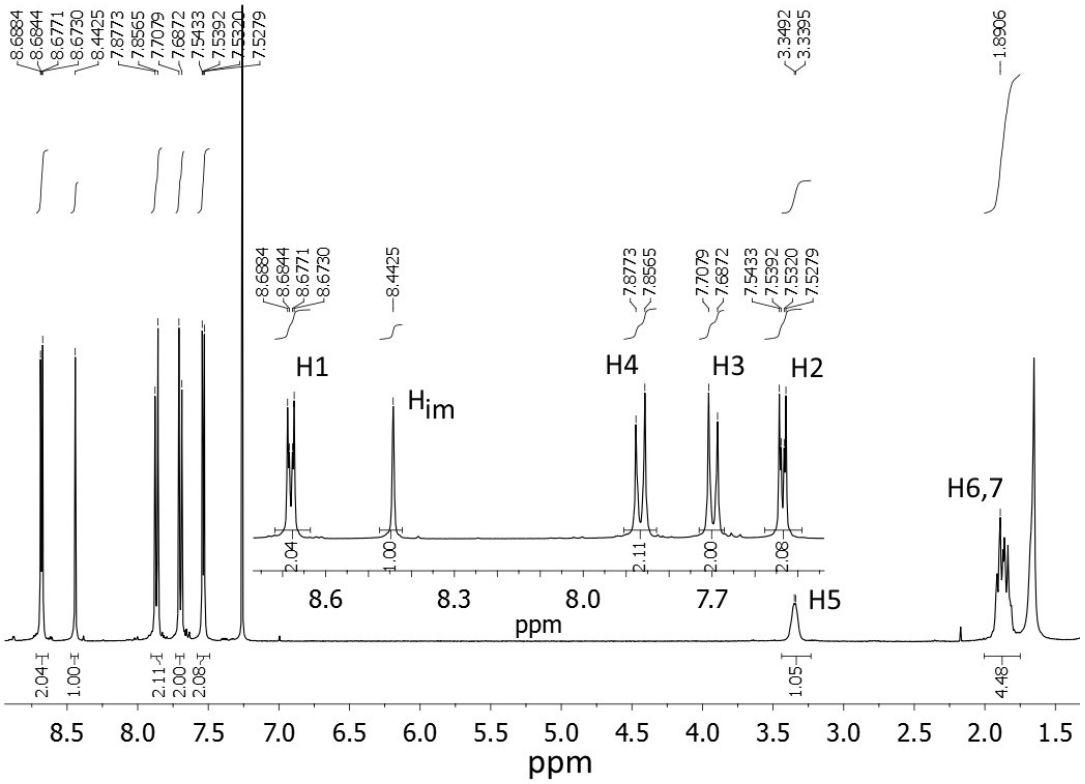

Figure S2. ^{1}H-NMR spectrum of **L**.

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.82, 150.49, 147.75, 140.18, 137.18, 128.96, 127.38, 121.73, 69.53, 32.69.

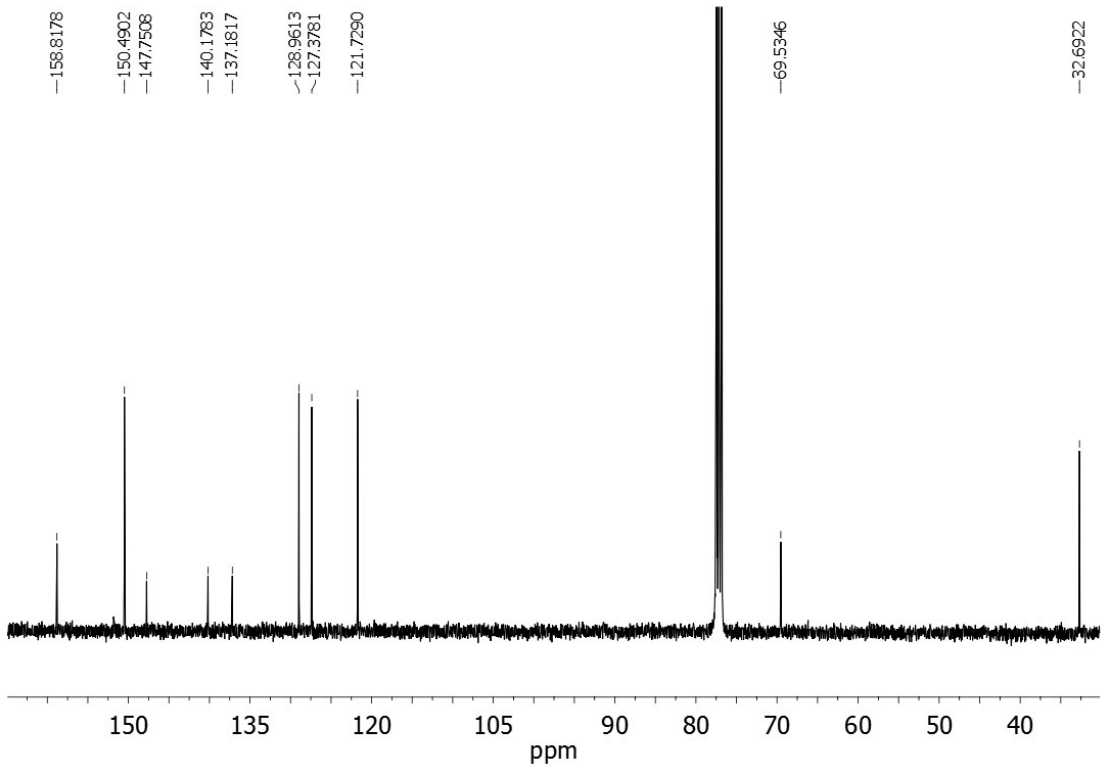

Figure S3. ^{13}C-NMR spectrum of **L**.

IR Experiments

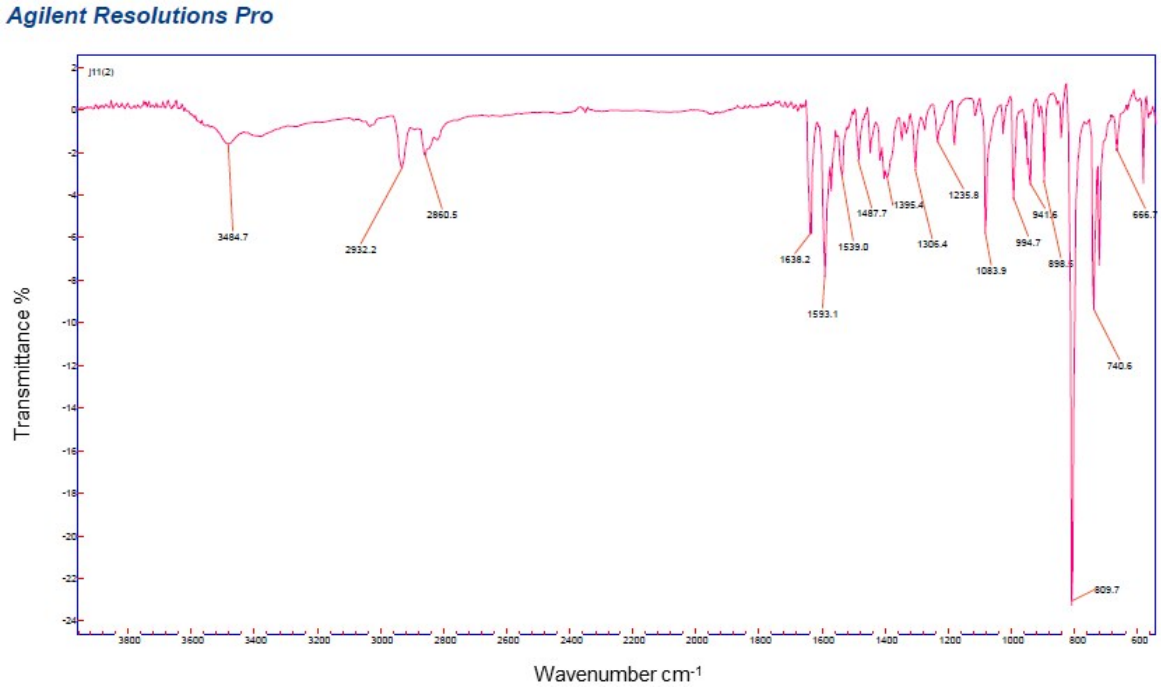

Figure S4. ATR-FTIR spectrum of **L**.

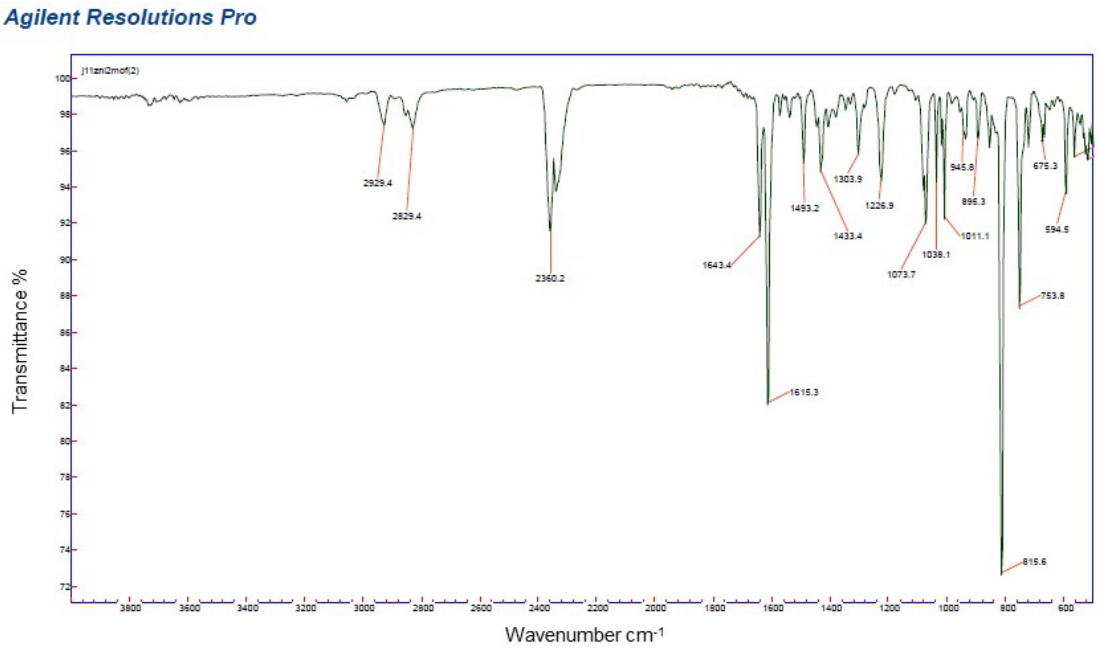

Figure S5. ATR-FTIR spectrum of **1**.

ESI-MS

ESI-MS: $[M]^+$ = 444.23 calcd. for C30H28N4, found 445.33 $[M+H]^+$

Single Crystal X-ray characterization of L

The single crystals of **L** were obtained by evaporating a $CHCl_3$ solution (5 mL) of L (20 mg) at room temperature. **L** crystal structure was determined by single crystal X-ray diffraction.

Table S1. Crystallographic data of **L**.

Crystal data for	**L**	
Empirical formula	$C_{30}\ H_{28}\ N_4$	
Formula weight	360.3210 g/mol	
Temperature	296(2)	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 10.4467(11) Å	α = 90.00 ˚
	b = 16.6677(17) Å	β = 99.288(7) ˚
	c = 14.0230(12) Å	γ = 90.00 ˚
Volume	2409.71(4) $Å^3$	
Z	4	
R- Factor (%)	5.58	
Density (calculated)	1.225 g/cm3	

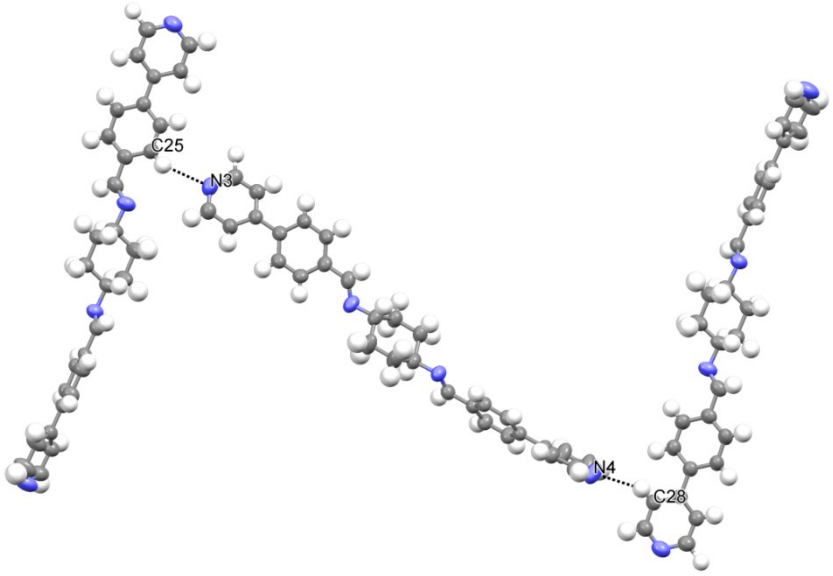

Figure S6. Crystal structure of **L** showing the weak intermolecular interactions hydrogen bond interactions between the C-H···N interactions.

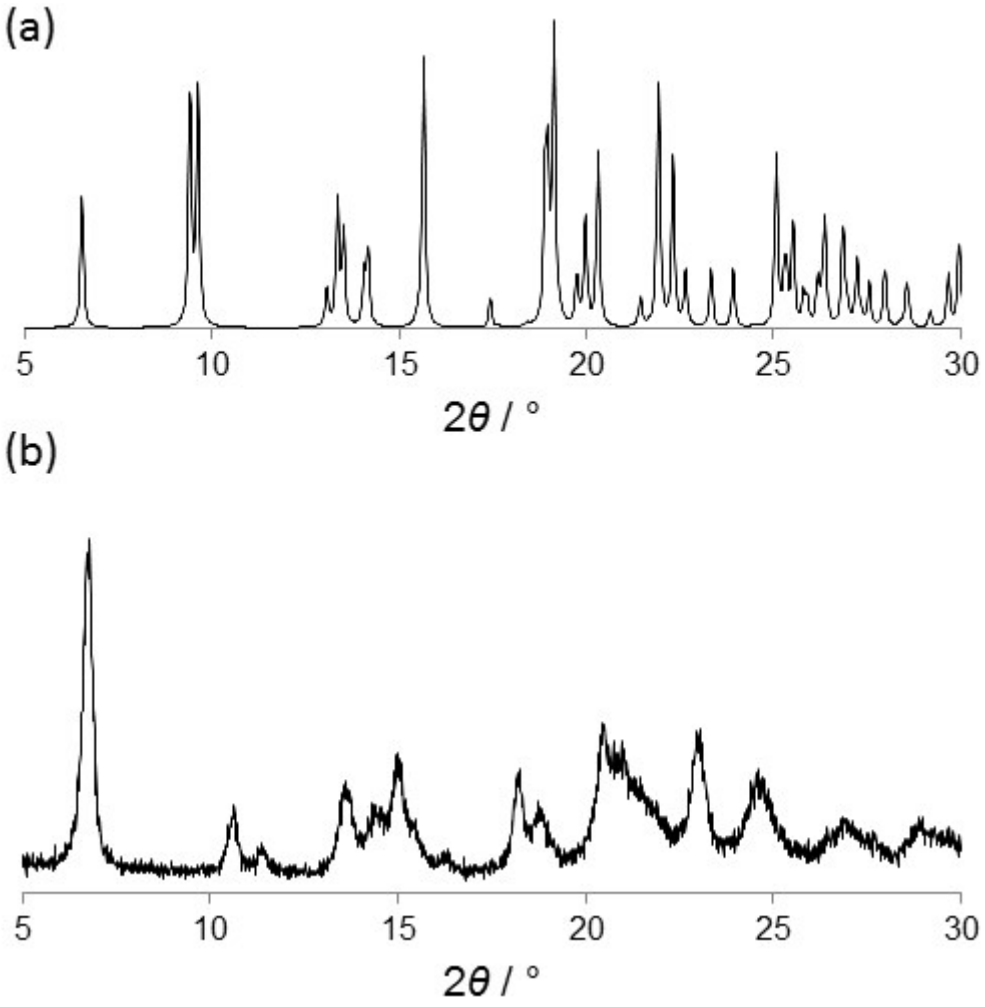

Figure S7. XRPD pattern of **1·CHCl$_3$** simulated from single crystal X-ray diffraction (100 K) (a); and experimental XRPD obtained by leaving single crystals of **1·CHCl$_3$** in contact with air for 30 mins. (300 K) (b).

Ab initio XRPD structure solution of 1.

The powder X-ray diffraction data of **1** were recorded at ambient temperature in transmission mode on a Bruker D8 diffractometer [Cu$K_{\alpha 1}$, Ge monochromated, linear position-sensitive detector covering 12˚ in 2θ; 2θ range, 5˚ -70 ˚; step size, 0.017˚; data collection time, 12 h. The sample was covered using transparent foil]. The XRPD data was used to carry out the crystal structure determination using DASH program.

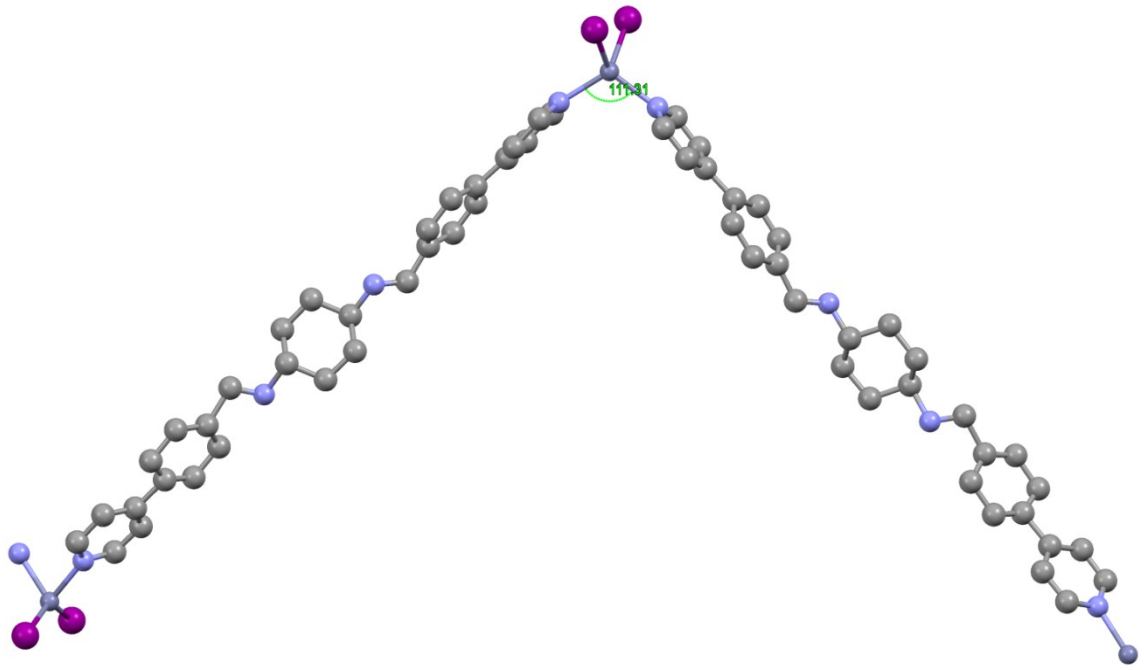

Figure S8. Ab initio crystal structure of **1** showing the V-shape geometry of the 1D coordination polymer chain.

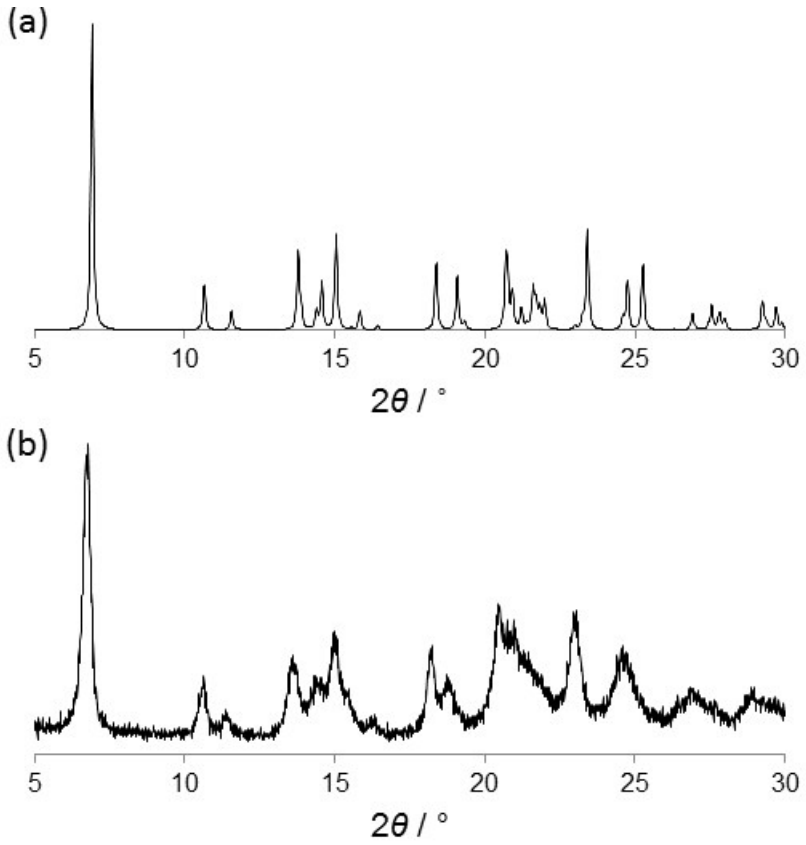

Figure S9. (a) Simulated XRPD pattern of **1** (300 K); (b) experimental XRPD pattern of **1** obtained after fast precipitation of a solution of **L** ($CHCl_3$) and a solution of ZnI_2 (MeOH).

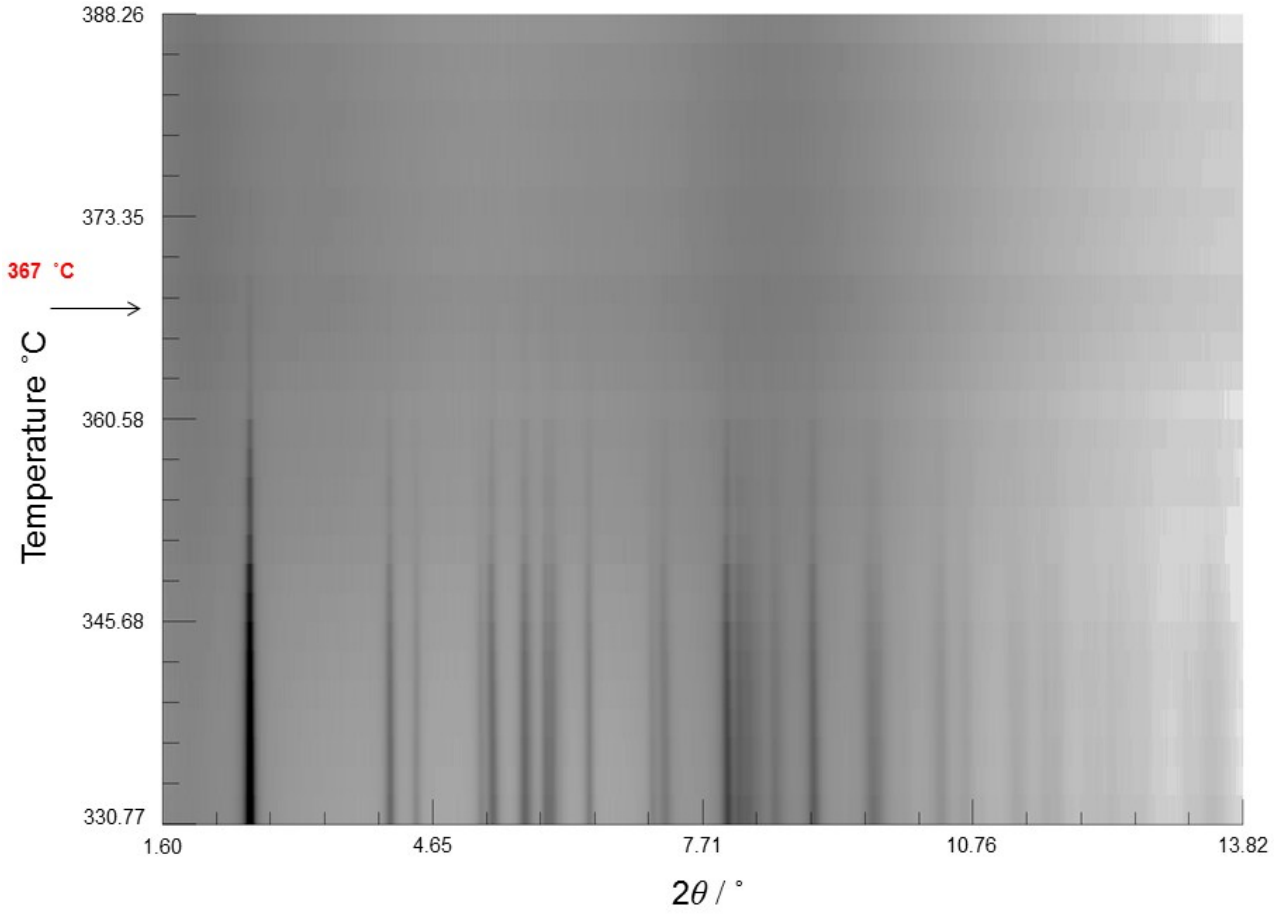

Figure S10. *In situ* high temperature experiments in which **1** was heated from RT to 450 ˚C. The heating rate was in two ramps: The first heating ramp from RT to 250 ˚C was a fast heating rate of 10 ˚C/min in which no phase transition was detected (*i.e.*, only thermal expansion). Once the sample reached 250 ˚C the heating rate was decreased to 4 ˚C/min. Clearly, **1** diffracts up to 360 ˚C and it becomes amorphous after that. The thermal stability of **1** is quite good for a 1D coordination polymer. Synchrotron radiation: Wavelength: 0.61996808Å.

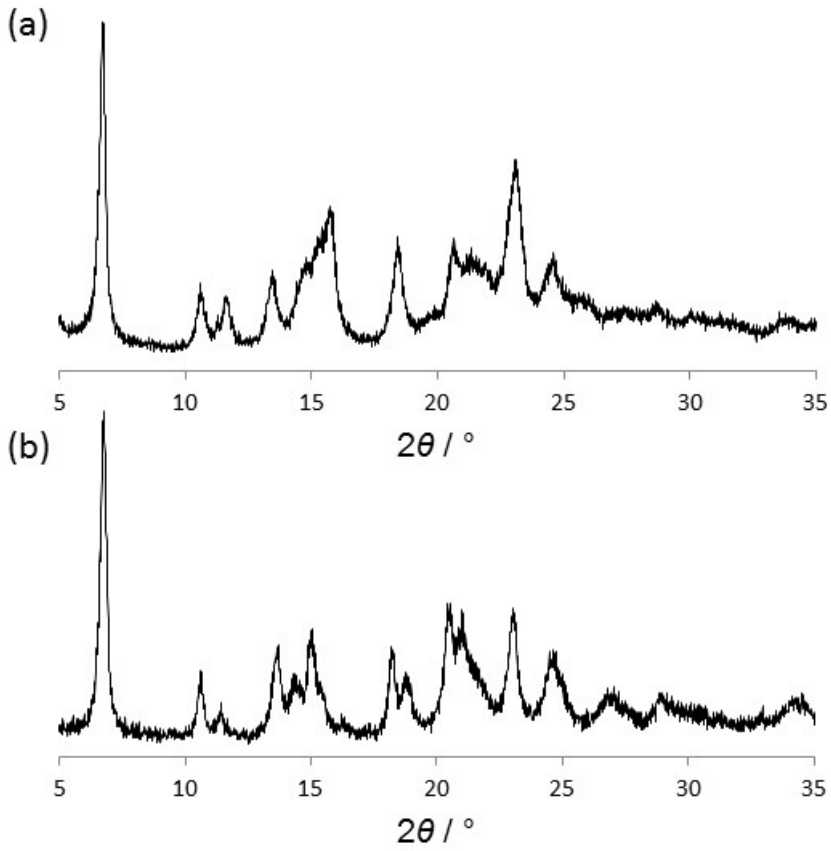

Figure S11. (a) XRPD pattern obtained after instant synthesis of **L** and $ZnBr_2$ in $CHCl_3$; (b) experimental XRPD pattern of **1** obtained after the instant synthesis of **L** and ZnI_2.

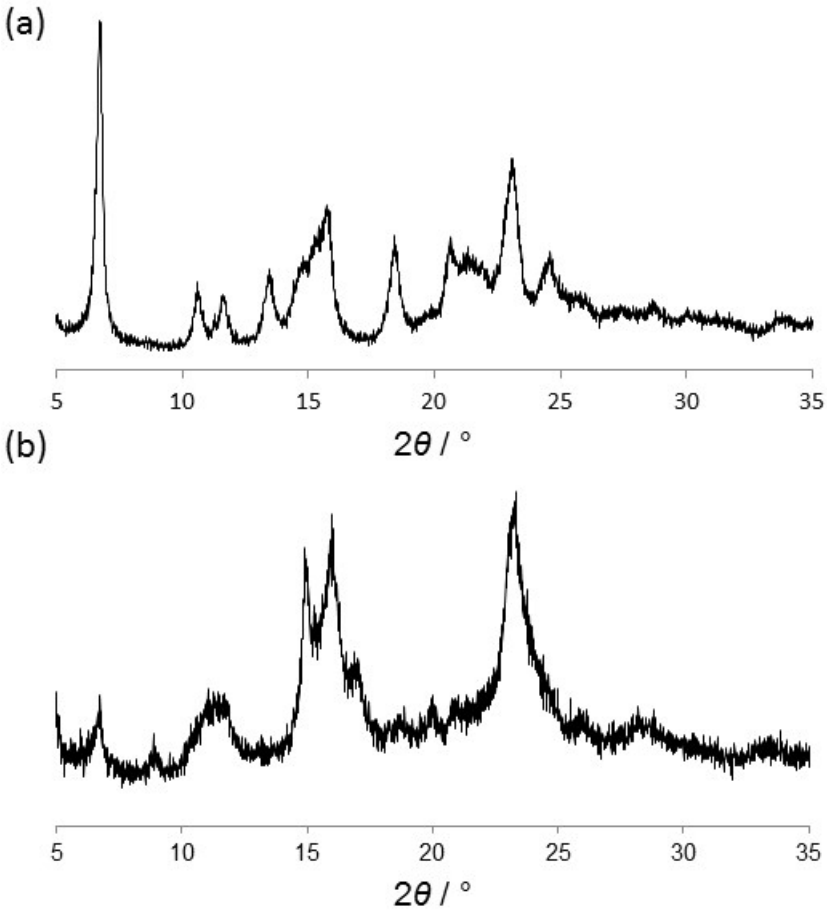

Figure S12. (a) XRPD pattern obtained after instant synthesis of **L** and $ZnBr_2$ in $CHCl_3$; experimental XRPD pattern of **1** obtained after the instant synthesis of **L** and $ZnCl_2$ (a).

SHG Experiments Set Up

The laser source is a Ti:Sapph laser emitting 150 fs pulses at a repetition rate of 80 MHz. The sample was excited thanks to a home-built microscope working in reflectance geometry; the excitation wavelength was 800 nm. For these measurements the microscope was equipped with a dichroic mirror 750 nm short pass and an objective providing 20× magnification. The signal coming from the sample was cleaned from the pump wavelength thanks to a BG39 coloured filter and then sent to a spectrometer. The thus dispersed light was collected thanks to a Streak Camera (Hamamatsu) detector, used for its high sensitivity.

MEASUREMENTS

Meas. 1: Crystal 1 inside, then it blasted. Measurement parameters:

- Detector gain 36, 1000 exposures each of which lasts around 35ms

Meas. 2: outside the crystal, just on oil. Measurement parameters:

- Detector gain 54, 1000 exposures each of which lasts around 35ms

Meas. 3: inside a crystal of urea, lower excitation power was used. Measurement parameters:

- Detector gain 36, 1000 exposures each of which lasts around 35ms

Meas. 4: inside the same crystal of urea, same power used for Meas.1 and 2 but the collected signal was attenuated with a 1 OD filter so to use the same gain as for Meas.1

- Detector gain 36, 1000 exposures each of which lasts around 35ms, 1OD filter

checkCIF (basic structural check) running

checkCIF/PLATON (basic structural check)

Structure factors have been supplied for datablock(s) j11

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No syntax errors found. CIF dictionary
Please wait while processing .... Interpreting this report
Structure factor report

Datablock: j11

Bond precision: C-C = 0.0033 A Wavelength=1.54178

Cell: a=10.4431(6) b=16.6727(9) c=14.0282(8)

alpha=90 beta=99.453(4) gamma=90

Temperature: 296 K

	Calculated	Reported
Volume	2409.4(2)	2409.3(2)
Space group	P 21/n	P21/n
Hall group	-P 2yn	?
Moiety formula	C30 H28 N4	?
Sum formula	C30 H28 N4	C30 H28 N4
Mr	444.56	445.57
Dx,g cm-3	1.226	1.228
Z	4	4
Mu (mm-1)	0.566	0.566
F000	944.0	948.0
F000'	946.48	
h,k,lmax	12,19,16	12,19,16
Nref	4343	4216
Tmin,Tmax	0.934,0.945	0.920,0.946

```
Tmin'              0.919

Correction method= # Reported T Limits: Tmin=0.920
Tmax=0.946 AbsCorr = MULTI-SCAN

Data completeness= 0.971        Theta(max)= 67.510

R(reflections)= 0.0501( 2781)      wR2(reflections)= 0.1643( 4216)

S = 1.044             Npar= 307
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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

ABSTY02_ALERT_1_C An _exptl_absorpt_correction_type has been given without a literature citation. This should be contained in the _exptl_absorpt_process_details field. Absorption correction given as Multi-scan

PLAT029_ALERT_3_C _diffrn_measured_fraction_theta_full Low ..... 0.971 Note

PLAT043_ALERT_1_C Calculated and Reported Mol. Weight Differ by .. 1.01 Check

PLAT068_ALERT_1_C Reported F000 Differs from Calcd (or Missing)... Please Check

PLAT230_ALERT_2_C Hirshfeld Test Diff for N1 -- C28 .. 6.5 s.u.

PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L= 0.599 127 Report

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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

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

PLAT899_ALERT_4_G SHELXL97 is Deprecated and Succeeded by SHELXL 2014 Note

PLAT909_ALERT_3_G Percentage of Observed Data at Theta(Max) Still 39 %

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

5 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
1 ALERT type 2 Indicator that the structure model may be wrong or deficient
3 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if

necessary, seek expert advice.

Publication of your CIF in IUCr journals

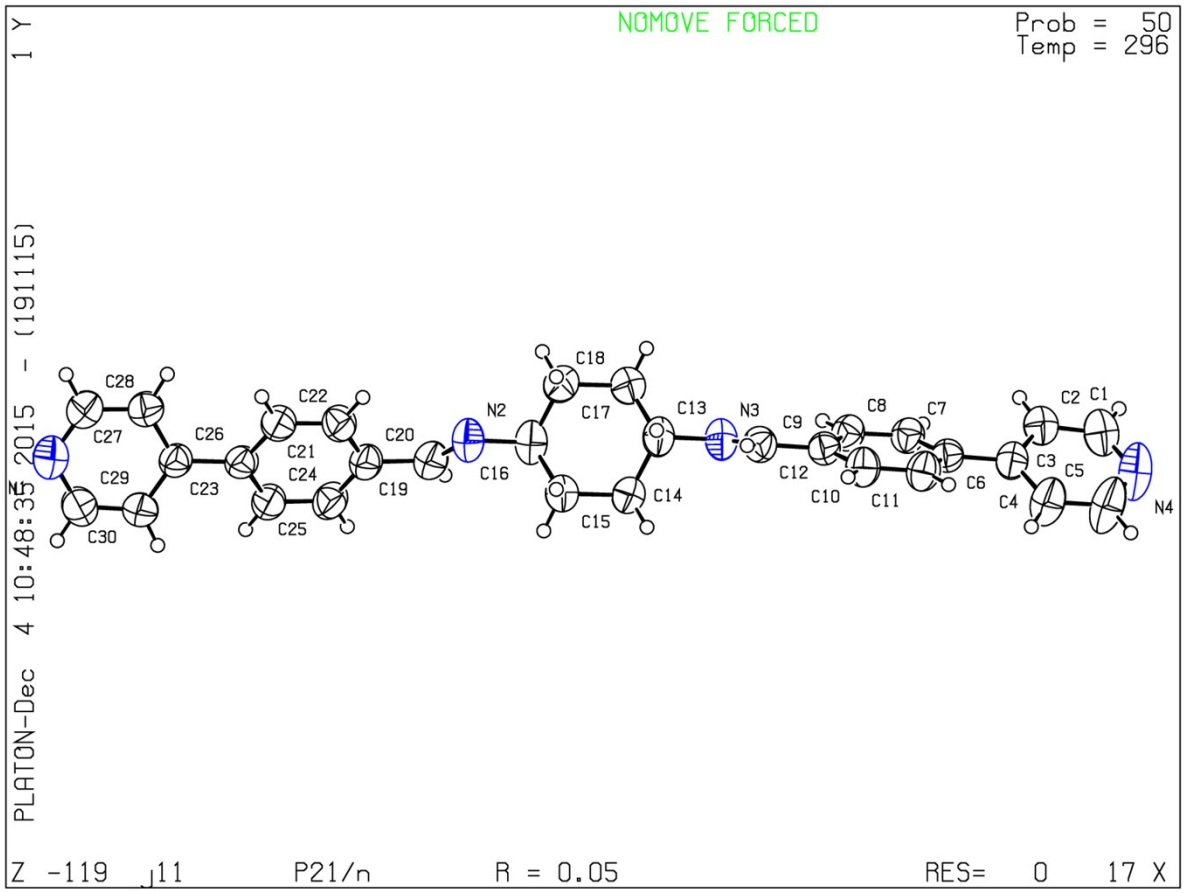
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 19/11/2015; check.def file version of 17/11/2015

Datablock j11 - ellipsoid plot



Download CIF editor (publCIF) from the IUCr
Download CIF editor (enCIFer) from the CCDC
Test a new CIF entry

checkCIF (basic structural check) running

checkCIF/PLATON (basic structural check)

Structure factors have been supplied for datablock(s) 1_CHCl3

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No syntax errors found. CIF dictionary
Please wait while processing .... Interpreting this report
Structure factor report

Datablock: 1_CHCl3

Bond precision: C-C = 0.0108 A Wavelength=1.54178

Cell: a=19.7541(13) b=7.1001(5) c=28.463(2)

alpha=90 beta=108.329(4) gamma=90

Temperature: 100 K

	Calculated	Reported
Volume	3789.6(5)	3789.6(5)
Space group	C 2/c	C2/c
Hall group	-C 2yc	?
Moiety formula	C30 H28 I2 N4 Zn, 2(C H Cl3)	?
Sum formula	C32 H30 Cl6 I2 N4 Zn	C32 H30 Cl6 I2 N4 Zn
Mr	1002.49	1002.47
Dx,g cm-3	1.757	1.757
Z	4	4
Mu (mm-1)	17.809	17.809
F000	1952.0	1952.0
F000'	1955.98	
h,k,lmax	23,8,33	23,8,33
Nref	3343	3271
Tmin,Tmax	0.472,0.490	0.470,0.536

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Correction method= # Reported T Limits: Tmin=0.470
Tmax=0.536 AbsCorr = MULTI-SCAN

Data completeness= 0.978        Theta(max)= 66.310

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S = 1.160             Npar= 204
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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

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PLAT029_ALERT_3_C _diffrn_measured_fraction_theta_full Low ..... 0.978 Note

PLAT342_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.0108 Ang.

PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd. # 1 Note
C30 H28 I2 N4 Zn

PLAT906_ALERT_3_C Large K value in the Analysis of Variance ..... 2.927 Check

PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L= 0.594 72 Report

PLAT934_ALERT_3_C Number of (Iobs-Icalc)/SigmaW > 10 Outliers .... 1 Check

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Alert level G

PLAT004_ALERT_5_G Polymeric Structure Found with Maximum Dimension 1 Info

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

PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large 51.36 Why ?

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

PLAT899_ALERT_4_G SHELXL97 is Deprecated and Succeeded by SHELXL 2014 Note

PLAT909_ALERT_3_G Percentage of Observed Data at Theta(Max) Still 85 %

PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Th(Min) ... 1 Report

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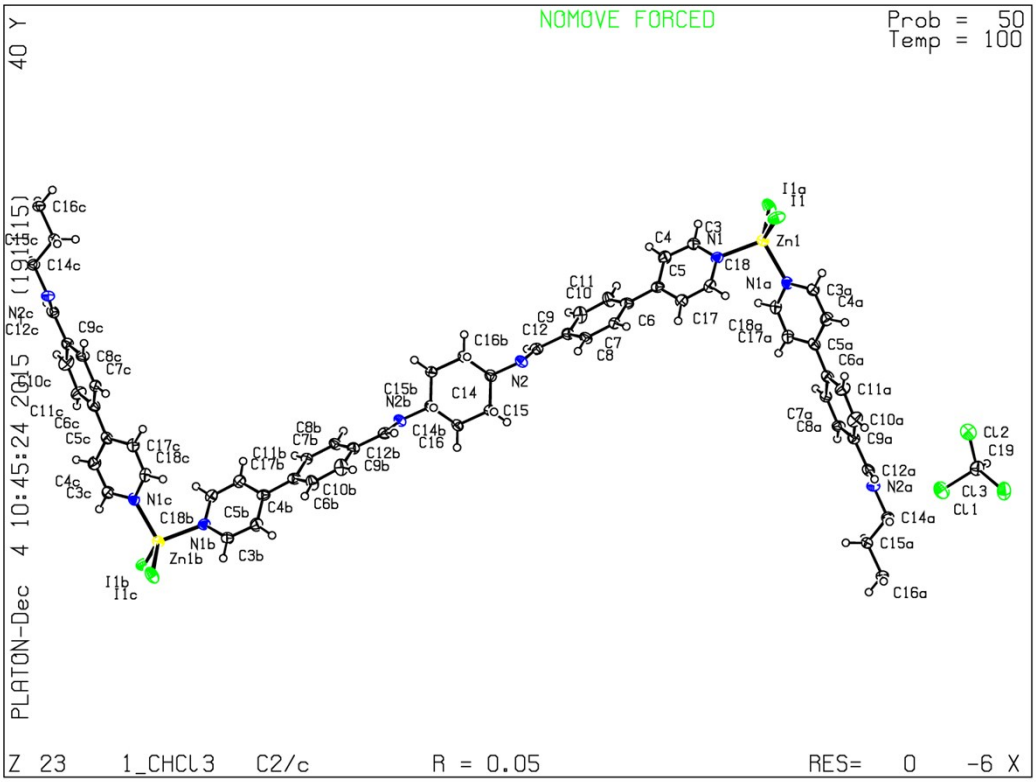
PLATON version of 19/11/2015; check.def file version of 17/11/2015

Datablock 1_CHCl3 - ellipsoid plot



Comments about the Absorbtion in 1·$CHCl_3$.

SADABS-2008/1 - Bruker AXS area detector scaling and absorption correction was used. *R*(int) was 0.0939 before and 0.0574 after correction. The Ratio of minimum to maximum transmission is 0.7659. The \l/2 correction factor is 0.0015.