Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Water-assisted assembly of (*E*)-arylvinylpyridine hydrochlorides: effective substrates for solid-state [2+2] photodimerization

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1. General

Melting points were determined with a Yanaco model MP microscope. Column chromatography was carried out using Merck silica gel 60 N. TLC was carried out on a Merck silica gel 60 PF_{254}. IR spectra were obtained on PERKIN ELMER SPECTRAM 2000 spectrometer as neat films between NaCl plates, or KBr pellets. NMR spectra were recorded on JEOL EX-400 spectrometer. ^{1}H NMR spectra were obtained at 400 MHz as dilute solution in $CDCl_3$, and the chemical shifts were reported relative to internal TMS. Low-resolution mass spectra were recorded at ionizing voltage of 70 eV by electron impact. X-Ray measurements were made on a Rigaku RAXIS RAPID II imaging plate area detector with graphite monochromated Cu-Kα radiation. All calculations were performed using the CrystalStructure crystallographic software package except for refinement, which was performed using SHELXL-97. Powder X-ray diffraction profiles were recorded using a Regaku Ultima IV with monochromated Cu-Ka radiation (λ = 1.54184 A, 50 kV, 40 mA, scan speed 2.0°/min, scan range 4 - 60°) equipped with a cross-beam optics system consisting of a PSA100U parallel slip analyzer. Thermogravimetric Analyses were carried out using a TG-DTA200SA instrument manufactured by Bruker. UV irradiation was performed using a 250 W high-pressure mercury lamp (ASAHI SPECTRA REX-250).

2. General procedure for irradiation of **1a**, **1b**, **1a**·HCl, **1b**·HCl, **1a**·HCl·2H_2O and **1b**·HCl·3H_2O

The powdered crystals (30 mg) placed between two glass plates were irradiated with 250W high-pressure mercury lamp for 0.5-16 h. The product was collected and was neutralized with saturated $NaHCO_3$ solution. This was extracted with CH_2Cl_2 and dried over anhydrous $MgSO_4$. Evaporation of the organic solvent gave a crude product, which was separated by thin layer chromatography using a 7:2:1 mixture of ethyl acetate, hexane and metanol as an eluent solvent.

3. Spectral data for 2b-4b

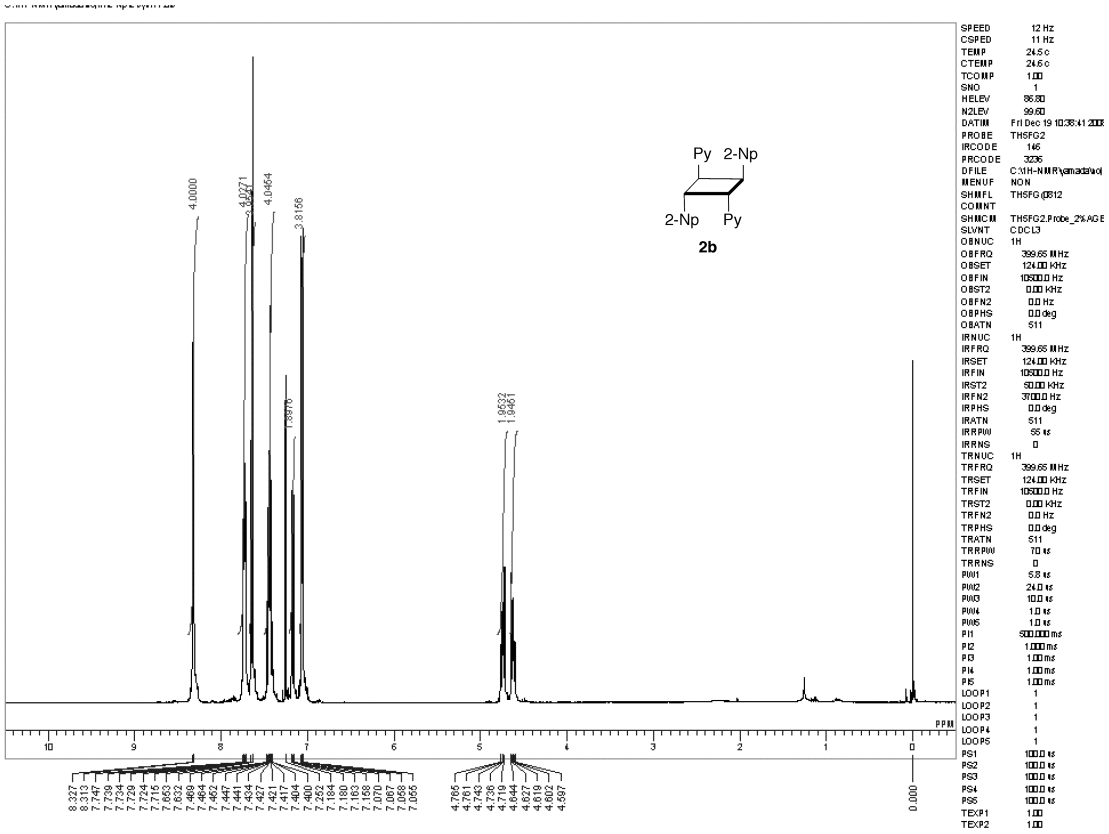
Compound **2b**: Pale yellow crystal (recrystallization from dichloromethane and benzene); mp 196-197 ℃; IR (KBr) 3018, 1597, 1552, 1509, 1414, 994, 861, 813, 763 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 5.6 Hz, 4H), 7.72-7.75 (m, 4H), 7.63-7.65 (m, 4H), 7.42-7.45 (m, 4H), 7.17 (dd, J = 8.6, 2.0 Hz, 2H), 7.06-7.07 (m, 4H), 4.72-4.77 (m, 2H), 4.60-4.64 (m, 2H); MS *m/z* 462 (M^+, 0.55%), 232 (20), 231 (100), 230 (64), 203 (8), 202 (13), ; HRMS calcd for $C_{34}H_{27}N_2$ 463.21742, $(M+H)^+$, found 463.21750.

Compound **3b**: Pale yellow crystal (recrystallization from dichloromethane and ether); mp 113-114 ℃; IR (KBr) 3053, 2972, 1599, 1508, 1422, 1115, 995, 820, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 4.4 Hz, 4H), 7.65-7.69 (m, 6H), 7.53 (d, J = 8.0 Hz, 2H), 7.34-7.42 (m, 4H), 7.15 (dd, J = 8.6, 2.0 Hz, 2H), 7.09 (d, J = 6.0 Hz, 4H), 4.66-4.70 (m, 4H); MS *m/z* 462 (M^+, 0.61%), 280 (26), 279 (18), 232 (39), 231 (100), 230 (96), 202 (13) ; HRMS calcd for $C_{34}H_{27}N_2$ 463.21742 $(M+H)^+$, found 463.21715.

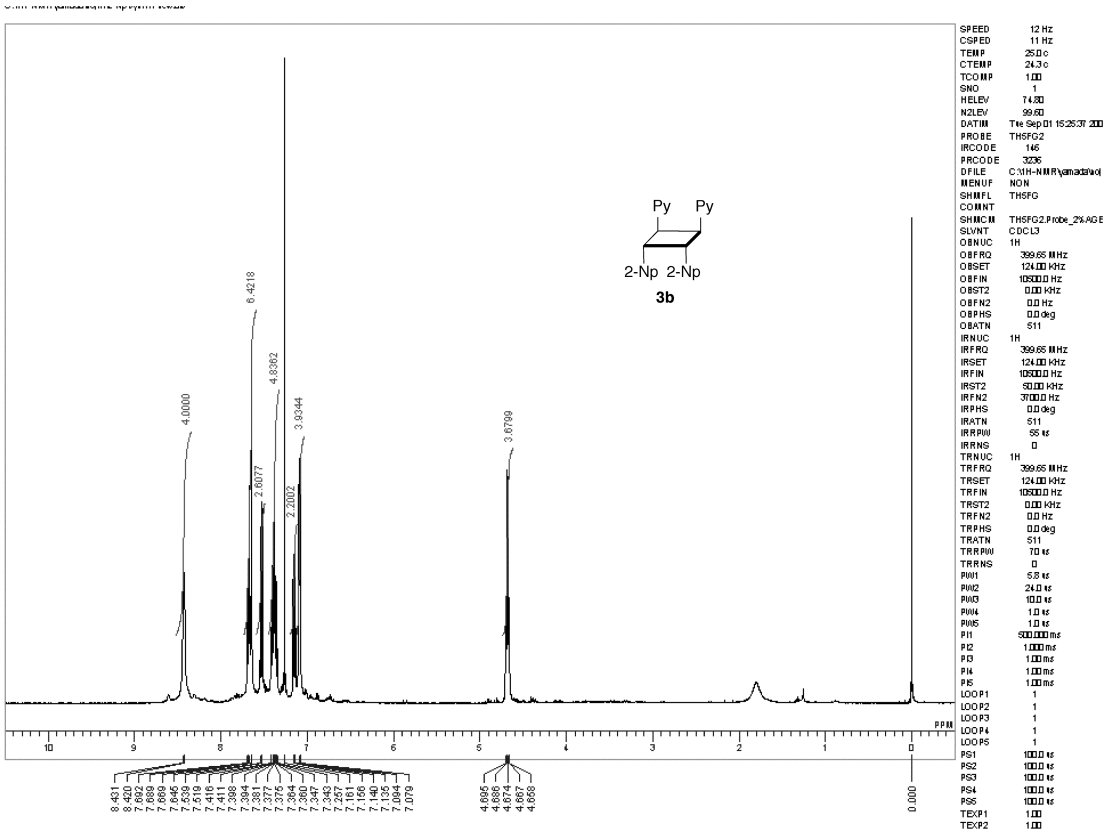
Compound **4b**: Pale yellow crystal (recrystallization from dichloromethane and ether); mp 225-226 ℃; IR (KBr) 3053, 2927, 1597, 1415, 1068, 817, 751 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 4.8 Hz, 4H), 7.80-7.89 (m, 8H), 7.46-7.52 (m, 6H), 7.21 (d, J = 6.0 Hz, 4H), 3.96-4.01 (m, 2H), 3.84-3.89 (m, 2H); MS m/z 462 (M^+, 1.2%), 232 (26), 231 (100), 230 (89), 202 (18) ; HRMS calcd for $C_{34}H_{27}N_2$ 463.21742 $(M+H)^+$, found 463.21560.

4. ^{1}H NMR spectra for 2b-4b

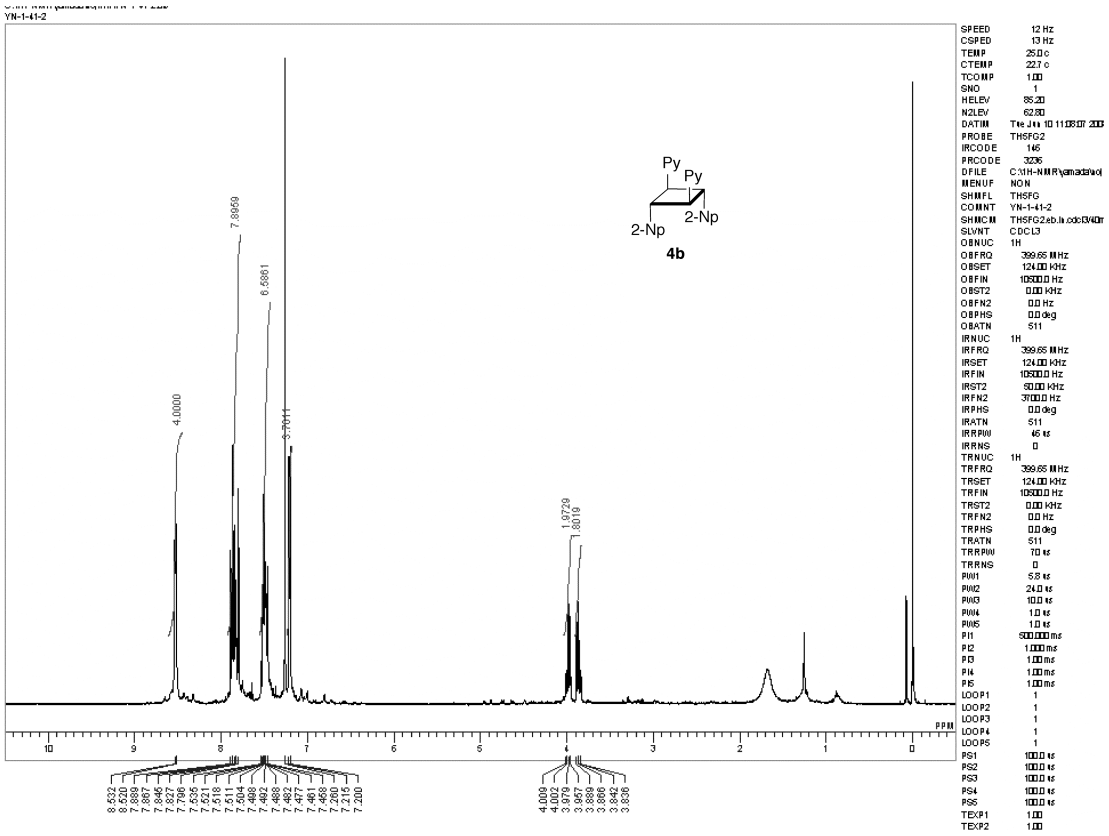
^{1}H NMR spectrum for **2b**



^{1}H NMR spectrum for **3b**



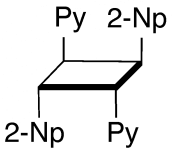
^{1}H NMR spectrum for **4b**

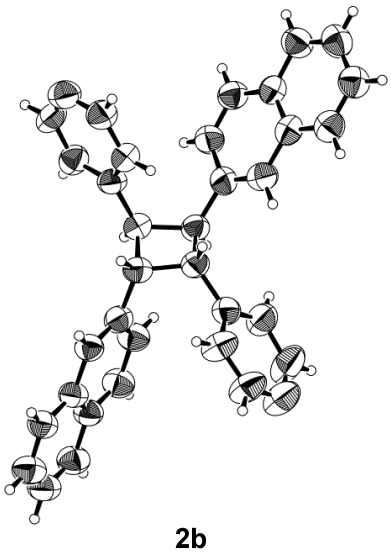


5. X-ray structural analyses of 2b and 4b, and packing diagram of 1a

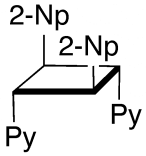
5-1.

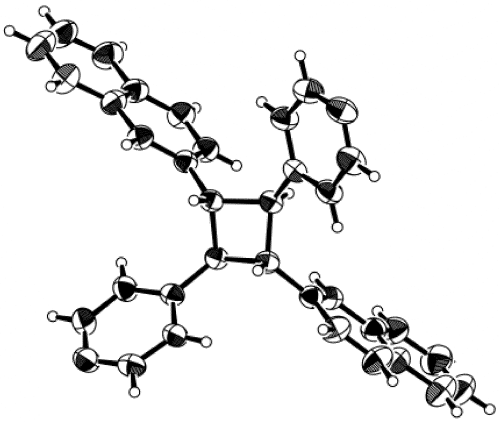
X-Ray Structures of **2b** and **4b**





2b





4b

Summary for X-ray structural analysis of **2b**

Formula: C(34)H(26)N(2)

******* Unit Cell Parameters *******		********* Model Refinement *********	
a:	10.5616(6)	R factor[all data]:	0.1488
b:	9.5453(6)	R1 factor[I>2.0sigma(I)]:	0.0761
c:	13.5147(7)	Rw factor[all data]:	0.2912
alpha:	90.000	goodness of fit:	1.064
beta:	110.173(2)	# of observations:	4523
gamma:	90.000	# of variables:	328
volume:	1278.89(12)	refl/para ratio:	13.8
		maximum shift/error:	1.01
		Refinement program:	SHELXL
		Refinement mode:	Single
		Flack Parameter:	0.0(19)

****** Space Group Information *****		****** Reflection Corrections ******	
symbol:	P21	absorption applied:	No
number:	4	abs. type:	SYM
centricity:	acentric	abs. range:	0.867-1.000
Z value:	2	decay applied:	No
formula weight:	462.59	decay (%):	0.00
calculated density:	1.201	redundants averaged:	No
mu (cm-1):	5.350		
crystal system:	monoclinic		
laue group:	2/m		
lattice type:	P		

******* Reflection Processing ******		***** Experimental Information ****	
total # processed:	14679	radiation:	Cu
total # unique:	4523	wavelength:	1.5419
R merge (%):	4.04	max. 2theta:	136.3
Wilson B:	7.37	sin(theta)/lambda:	0.6021
		temperature (C):	25.0

Summary for X-ray structural analysis of **4b**

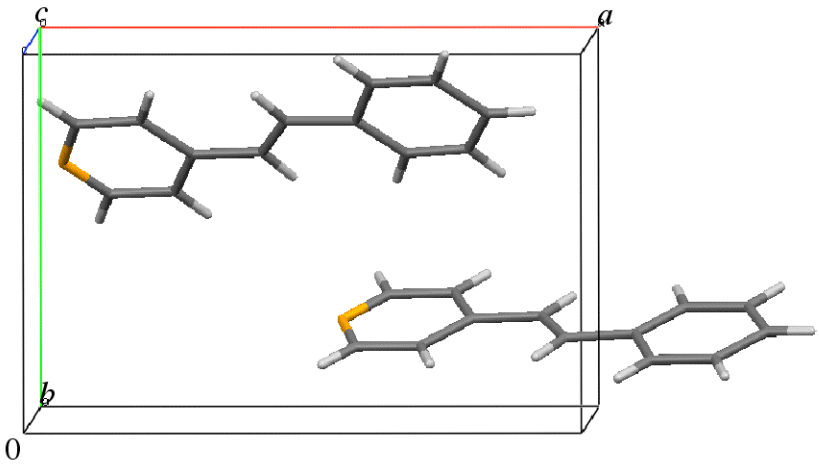
Formula: C(34)H(26)N(2)

******* Unit Cell Parameters *******		********* Model Refinement *********	
a:	22.5434(4)	R factor[all data]:	0.1466
b:	8.91677(10)	R1 factor[I>2.0sigma(I)]:	0.0648
c:	49.7495(10)	Rw factor[all data]:	0.2166
alpha:	90.000	goodness of fit:	1.036
beta:	90.000	# of observations:	9132
gamma:	90.000	# of variables:	651
volume:	10000.4(3)	refl/para ratio:	14.0
		maximum shift/error:	0.00
		Refinement program:	SHELXL
		Refinement mode:	Single

****** Space Group Information *****		****** Reflection Corrections ******	
symbol:	Pbca	absorption applied:	No
number:	61	abs. type:	SYM
centricity:	centric	abs. range:	0.847-1.000
Z value:	12	decay applied:	No
formula weight:	462.59	decay (%):	0.00
calculated density:	0.922	redundants averaged:	No
mu (cm-1):	4.105		
crystal system:	orthorhombic		
laue group:	mmm		
lattice type:	P		

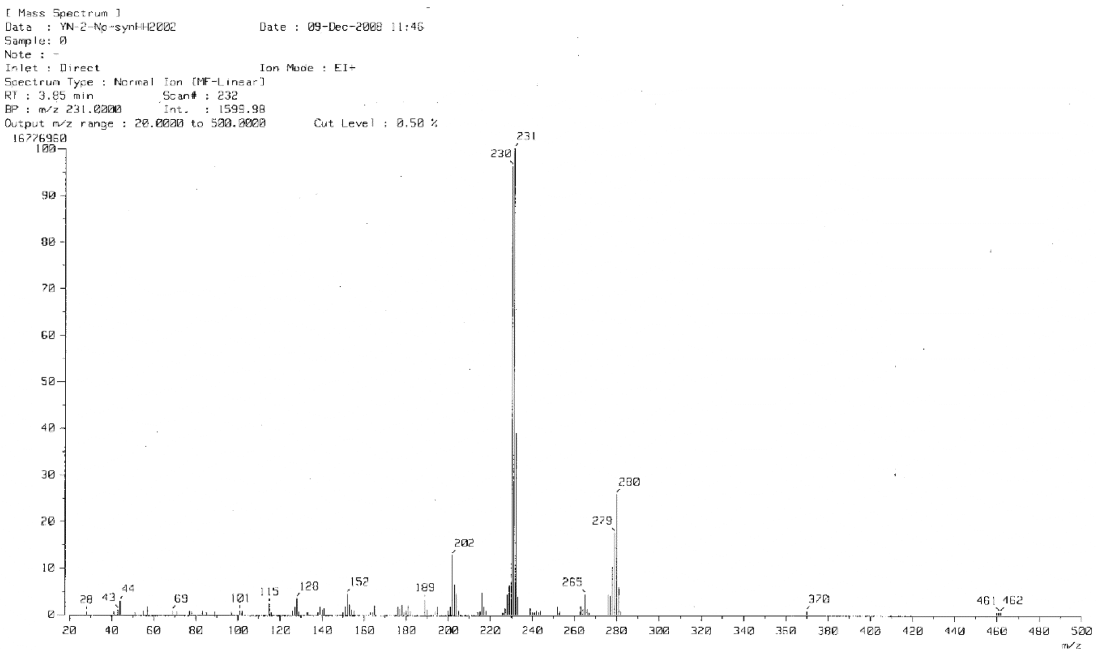
******* Reflection Processing ******		***** Experimental Information ****	
total # processed:	104123	radiation:	Cu
total # unique:	9132	wavelength:	1.5419
R merge (%):	6.90	max. 2theta:	136.4
Wilson B:	4.48	sin(theta)/lambda:	0.6022
		temperature (C):	25.0

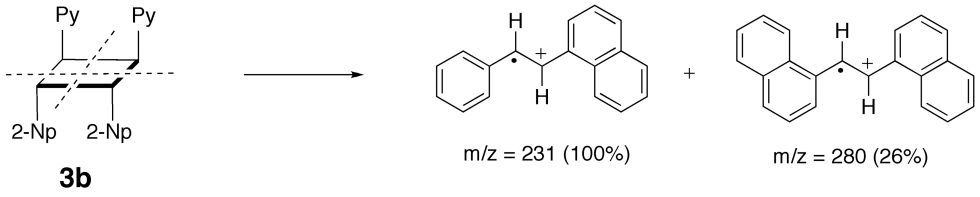
5-2. X-ray packing diagram of 1a



6. MS spectrum for 3b

MS spectrum of **3b**





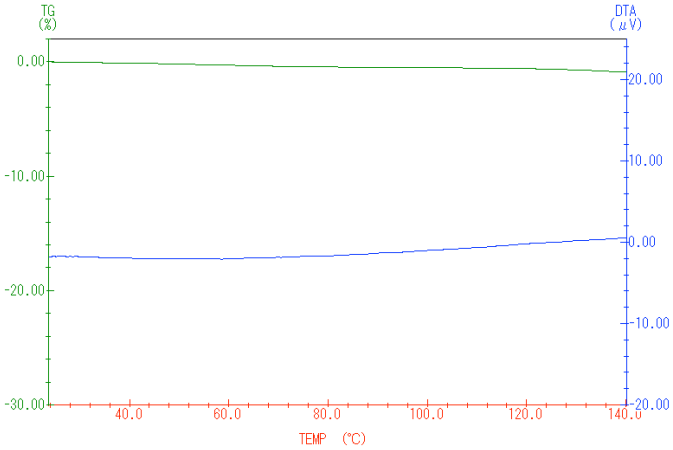
3b

Determination of a head-to-head structure of **3b**

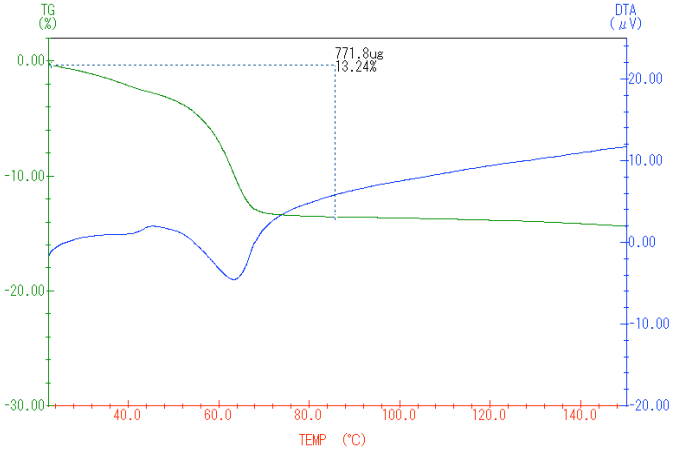
7. TG/DTA profiles

7-1. TG/DTA profiles for 1a·HCl at 58% relative humidity

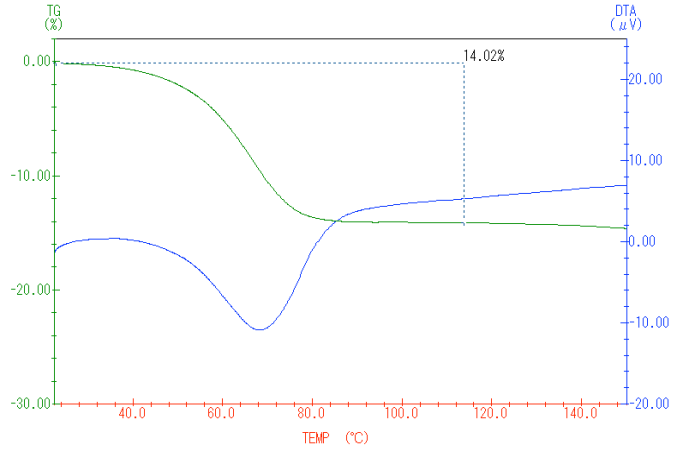
0h



24h

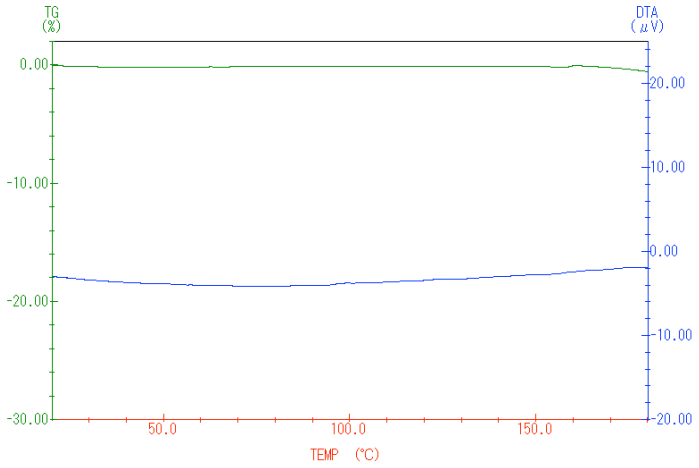


48h

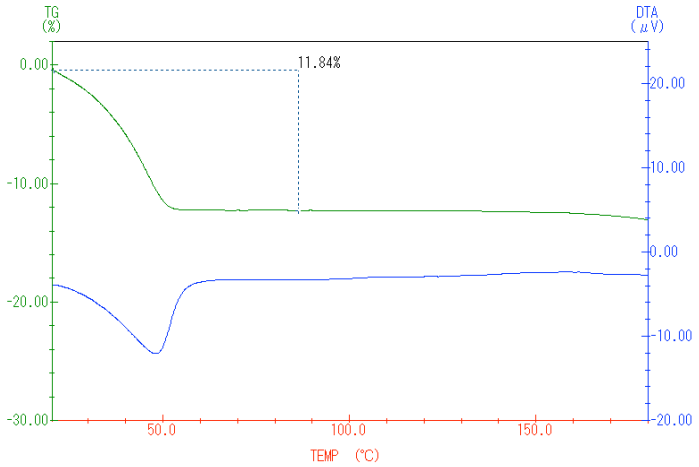


7-2. TG/DTA profiles for 1b·HCl at 58% relative humidity

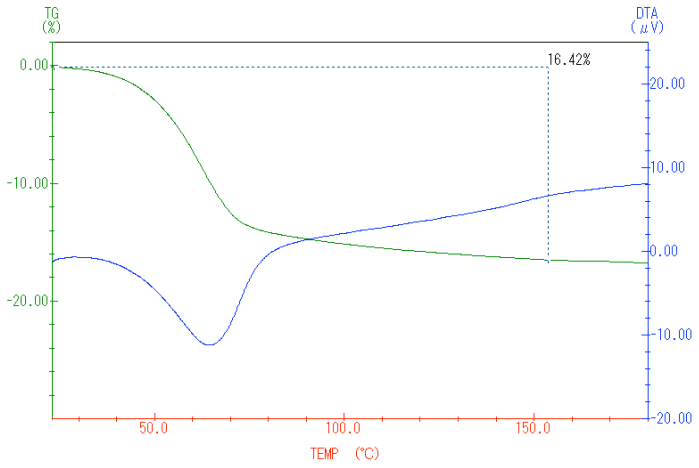
0h



2days



6days



8. PXRD patterns for **1b**·HCl·$3H_2O$, **1b**·HCl and **1b**·HCl at relative humidity of 58%