Electronic Supporting Information

Cobalt-based Metal-Organic Framework for Desulfurization of Thiophene as a Model Fuel.

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Material and Methods

Thiophene was procured from Avra chemical, Iso-octane solvent was obtained from SRL (Sisco Research Laboratories, India) Cobalt Nitrate hexahydrate [$Co(NO_3)_2.6H_2O$] was purchased from SRL, biphenyl-4,4'- dicarboxylic acid (bpdc) and 4,4'-bipyridine (bpy) were purchased from TCI chemicals.

The thiophene quantification was analyzed using Jasco-V650 UV-vis spectrophotometer at 230 nm for thiophene with 10 mm path length quartz cells. Functional groups analysis was performed using Attenuated total reflectance (ATR) Alpha II spectrometer, a compact FT-IR spectrometer with a room temperature DTGS1 detector. The crystal planes and XRD pattern of the MOF structure were studied using Rigaku Ultima- IV X-Ray diffractometer with Cu-Kα radiation (1.5405 Å) over 2θ range 5º and 40º. The surface morphology and elemental composition of the MOF were confirmed by SEM-EDX using FEI Apreo LoVac scanning electron microscope. XRF measurement was performed using PANalytical make Epsilon model -1. Surface characterizations, pore diameter and pore volumes of the MOF material were obtained from BET-N_2 isotherm analysis using Microtrac Bel (BEL SORP mini II) BET surface area analyser (degassed the samples at 120ºC for 4 h; N_2 adsorption). The elemental composition and its oxidation stated were analysed from X-ray Photoelectron spectroscopy

analysis using Thermo Scientific K-Alpha (Al-Kα monochromator) XPS instrument. The batch adsorption experimental studies were performed using Biotecnics orbital shaker.

Synthesis of BITSH-1 metal-organic framework.

To synthesize BITSH-1 MOF, $Co(NO_3)_2.6H_2O$ of 0.1 mmol concentration was reacted with 0.1 mmol of biphenyl-4,4'-dicarboxylic acid (bpdc) and 0.05 mmol of 4,4'-bipyridine in 10mL volume of dimethylformamide (DMF) at 130 ºC heating for 24 h. Followed by heating the purple-coloured MOF crystals were collected and washed thoroughly in ethanol and DMF solvent. The washed dried MOF sample was used for further characterization and application studies.[17]

Adsorptive desulfurization procedure

Desulfurization of thiophene in isooctane was carried out in conventional stirring method using Vortex shaker. In brief, 1000 mg L^{-1} of thiophene stock solution was prepared from which the working solutions of lower concentrations of 40 to 500 mg L^{-1} by appropriate dilutions were prepared. For adsorptive desulfurization of thiophene using BITSH-1, 10 mL of particular concentration of thiophene in isooctane was taken, to which 20 mg of the BITSH-1 adsorbent was added and sonicated for 10 minutes in a bath sonicator. After sonication, adsorption was performed in orbital shaker for 3 h at 100 rpm.

Concentration of thiophene in isooctane before and after adsorption was quantified using UV-vis spectrophotometer. The wavelength of thiophene at specific λ_{max} of 233nm corresponding to n to π^* transition of the lone of pair of electrons on the sulfur was used for quantification of thiophene. The equilibrium adsorption capacity was calculated as

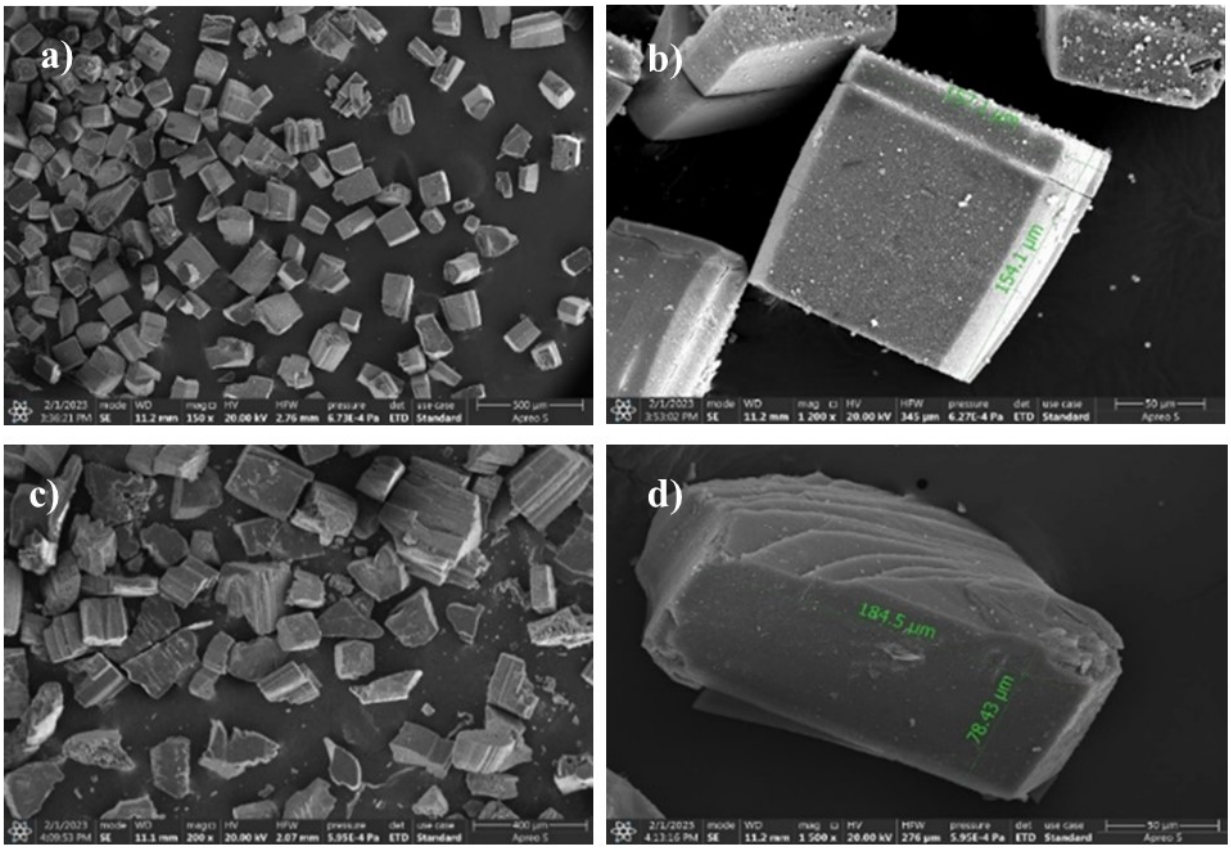
$$q_e = (C_o - C_e)\, V/W \qquad (1)$$

where C_o and C_e are the initial and final concentrations of thiophene, V is volume of the thiophene in Isooctane in L and W is the weight of MOF adsorbent taken in g.

Characterization of BITSH-1

Field Emission Scannning Electron Microscopy (FESEM)

The morphological nature of the MOF material was studied using SEM imgaes and the elemental compositions were confirmed by EDX spectra and elemental mapping.



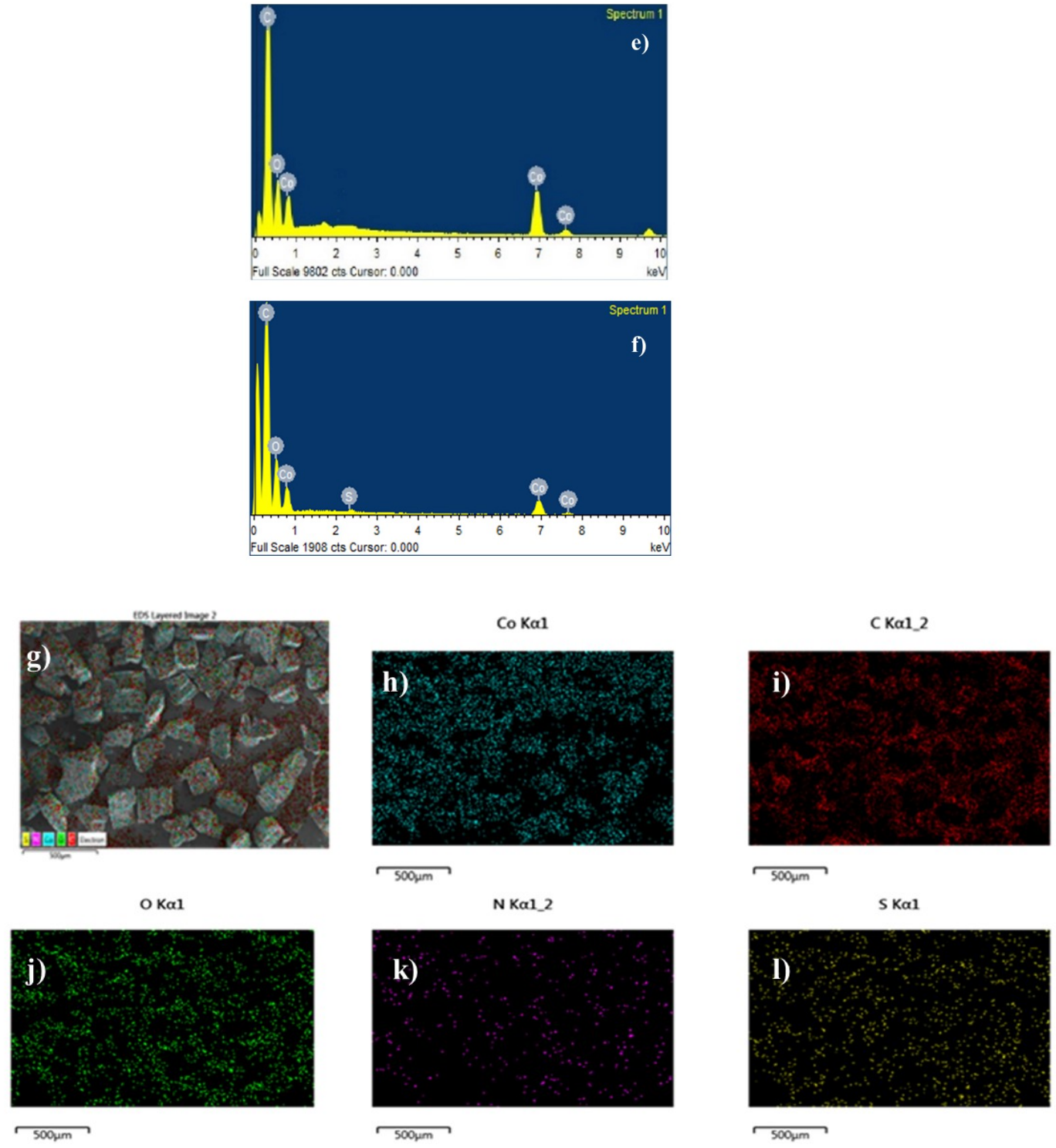


Fig. S1 a) &b SEM images of as synthesized BITSH-1, c)&d) SEM images of BITSH-1 after adsorption of thiophene, e) & f) EDX spectra of BITSH-1 before and after adsorption, g)-l) Elemental mapping of BITSH-1 with sulfur after adsorption

Powder X-ray Diffraction (PXRD)

The crystalline nature of the BITSH-1 before and after adsorption of thiophene was characterized using PXRD patterns between 2ɵ of 5 to 40º.

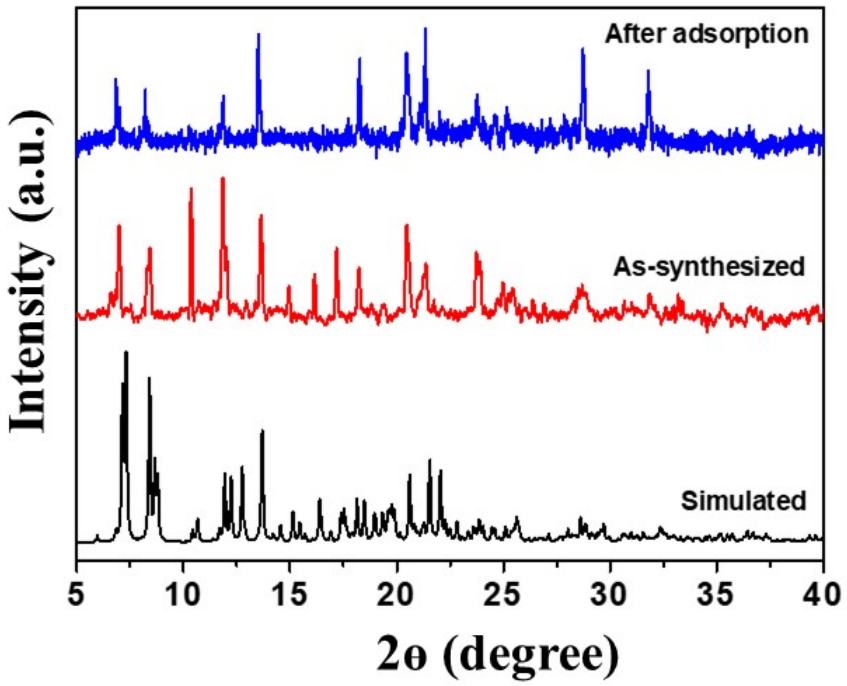


Fig. S2 XRD pattern of Simulated BITSH-1, as synthesized & after adsorption of thiophene

Nitrogen Adsorption Experiments

Surface properties of the MOF BITSH-1 such as specific surface area, pore volume and pore diameter were characterized by BET-N_2 isotherm with pre-treatment conditions for 120ºC for 4 h.

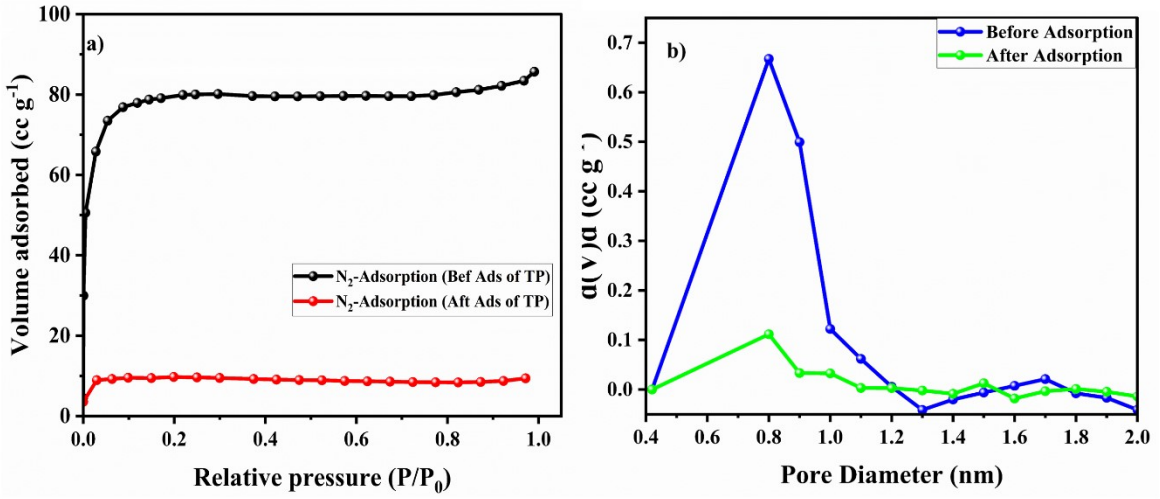


Fig. S3a) BET-N_2 Adsorption isotherm Plot & b) MP plot for BITSH-1 before and after adsorption of thiophene

Thermal Analysis

Thermal analysis of the BITSH-1 MOF before and after adsorption of thiophene was performed with Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) between 30 ºC and 800 ºC.

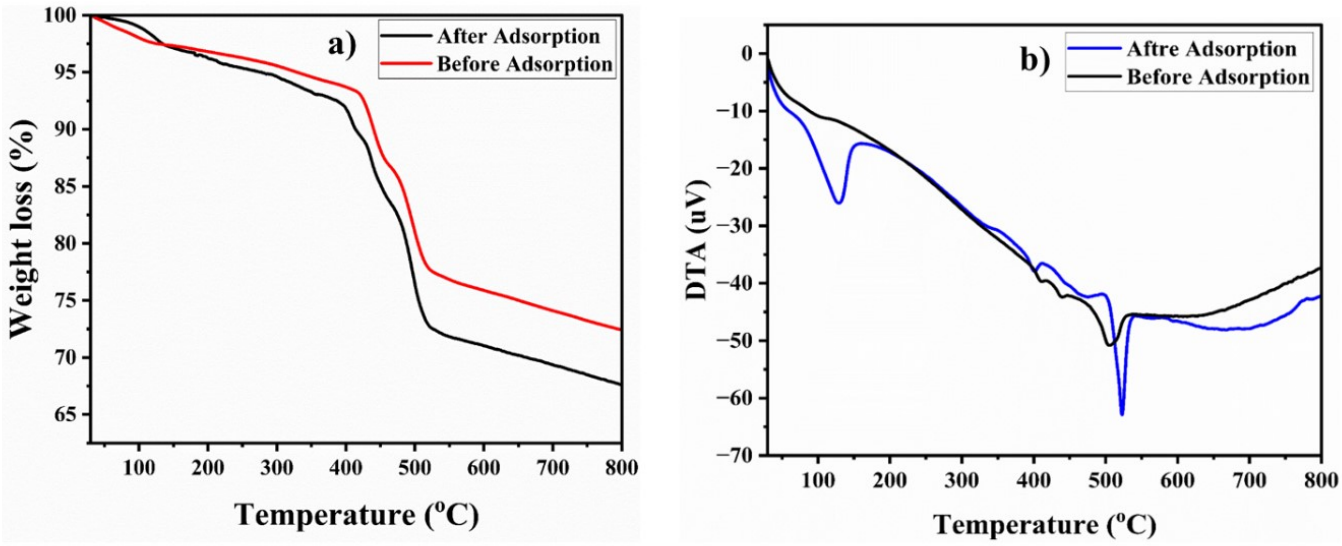


Fig. S4a) & b) TGA & DTA graph of BITSH-1 before and after adsorption

Tables

Table S1. Theoretically calculated Isotherm parameters from experimental data

Isotherm models	Isotherm parameters	Values
Langmuir	q_{max} (mg g^{-1})	**95.438**
	K_L (L mg^{-1})	0.026
	R^2	0.966
Freundlich	K_F ($mg^{1-1/n}$ g^{-1} $L^{1/n}$)	9.313
	n	2.338
	R^2	0.954
Temkin	b_T (J mol^{-1})	117.420
	K_T (L g^{-1})	1.835×10^{-1}
	R^2	0.881

Table S2. Theoretically obtained kinetics Parameters for adsorption of thiophene on BITSH-1

Kinetics models	Parameters	Values
pseudo–first order	k_1 (min^{-1})	0.031
	q_{e1} (mg g^{-1})	16.541
	R^2	0.964
pseudo–second order	k_2 (g mg^{-1} min^{-1})	0.099
	q_{e2} (mg g^{-1})	19.998
	R^2	0.995

Intra–particle diffusion	C_1 (mg g^{-1})	-0.985
	K_{i1} (mg g^{-1} min$^{1/2}$)	-1.834
	R^2	0.999
	C_2 (mg g^{-1})	4.261
	K_{i2} (mg g^{-1} min$^{1/2}$)	1.020
	R^2	0.960
	C_3 (mg g^{-1})	9.294
	K_{i3} (mg g^{-1} min$^{1/2}$)	0.665
	R^2	0.919

Table S3.

Theoretically calculated thermodynamic parameters for adsorption of thiophene on BITSH-1

Temperature (Kelvin)	ΔG^o (kJ mol^{-1})	ΔH^o (kJ mol^{-1})	ΔS^o (kJ mol^{-1} K^{-1})	R^2
298	-6.505	-88.004	-0.2762	0.9813
308	-1.254			
318	0.318			
328	1.748			

Single Crystal X-ray diffraction studies

The single crystal data was collected using a good quality single crystal of the MOF after exposure to thiophene/iso-octane solution. The data was collected at 135 K and the structure was solved using Olex2 software and refined using Olex2 function. The host framework does not show any disorder and the thermal parameters are good. The guest molecule, thiophene, on the other hand shows high thermal parameter values owing to the displacement of the thiophene molecules in the MOF channels. One of the thiophene molecules could be modelled with certainty and another thiophene molecule with a lower occupancy (~0.70) was squeezed using the mask function of Olex2 software.

Table S4. Single crystal data for BITSH-1-T structure containing thiophene inside the MOF pores.

Identification code	BITSH-1-T
Empirical formula	$C_{60}H_{40}Co_3N_2O_{12}S$
Formula weight	1189.858
Temperature/K	135
Crystal system	orthorhombic
Space group	Pbcn
a/Å	13.8970(2)
b/Å	26.1099(4)
c/Å	18.0592(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	6552.77(18)
Z	4
ρ_{calc}g/cm^3	1.206
μ/mm^{-1}	6.629
F(000)	2410.9
Crystal size/mm^3	0.2 × 0.1 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.36 to 159.7
Index ranges	-13 ≤ h ≤ 17, -33 ≤ k ≤ 32, -13 ≤ l ≤ 22
Reflections collected	27818
Independent reflections	7034 [R_{int} = 0.0354, R_{sigma} = 0.0334]
Data/restraints/parameters	7034/29/332
Goodness-of-fit on F^2	1.010
Final R indexes [I>=2σ (I)]	R_1 = 0.0622, wR_2 = 0.1827
Final R indexes [all data]	R_1 = 0.0677, wR_2 = 0.1884
Largest diff. peak/hole / e Å^{-3}	1.30/-0.95
CCDC number	2289319

The interactions between the host-guest molecules is shown below and the various distances of interaction and provided in table S5.

Table S5. Distances for the interactions of the thiophene molecule with BPDC and BPY linkers.

Interactions	Atoms	Distance (Å)
CH···O	H30 and O4	2.91
CH···O	H30 and O2	3.01

CH···O	H27 and O2	2.94
CH···HC	H27 and H3	2.80
CH···S	H26 and S1	3.25