

## Molecular structure characterization of bituminous coal in Northern China via XRD, Raman and FTIR spectroscopy

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### Abstract:

Bituminous coal is used widely for a variety of applications despite causing a range of problems within processes. The complexity and heterogeneity of the molecular structure of coal is one of the reasons for problems during use. Investigation into the molecular structure of the bituminous coal is reported from using X-ray diffraction (XRD), Raman spectroscopy, and Fourier

Transform infrared spectroscopy (FTIR) experiments on four coal samples from northern China.

The average lateral sizes ( $L_a$ ), stacking heights ( $L_c$ ) and interlayer spacing ( $d_{002}$ ) of the coal samples' crystallite structures derived from the XRD ranged from 25.78 to 27.93 Å, 17.27 to 25.88 Å and 3.40 to 3.52 Å, respectively; and the G-D<sub>1</sub>, I<sub>D1</sub>/I<sub>G</sub> and  $L_a$  of the samples ranged from 245.06 to 249.63 cm<sup>-1</sup>, 2.18 ~ 2.48 and 18.16 to 20.64 Å, respectively. The FTIR spectra reveals that coal samples incorporate oxygen-containing functional groups, aliphatic functional groups, aromatic functional groups and hydroxyl functional groups. Results show these four coal samples contained a low degree of ordered microcrystalline units with a low degree of aromatic conformation. The samples have the largest proportion of oxygenated functional groups, followed by aromatic structures, aliphatic structures and hydroxyl groups. Results from this study could inform the ongoing study of molecular structural characteristics of bituminous coal as well as help our understanding of properties such as wettability and pore structure.

**Key words:** Molecular structure; Bituminous coal; XRD; Raman spectroscopy; FTIR

## 34 1. Introduction

35 The coal industry is one of the pillars of the world's energy industry, as it provides abundant and  
36 widely distributed fossil energy resources for power generation [1]. There are notable difference in  
37 coal from ashless high calorific value material under constant humidity and volatile matter on dry ash  
38 free basis ( $V_{daf}$ ), coal is roughly divided into lignite, bituminous coal and anthracite. Currently,  
39 bituminous coal is widely used in coking, power generation, coal gasification, fuel, and fuel cells  
40 because of its easy combustion, low ash and moisture content, and high calorific value. Coal is mainly  
41 a complex three-dimensional structure composed of fused aromatic moieties [2]. This highly complex  
42 substance composed of minerals that reflect the sedimentary environment and nature of organic  
43 precursors, complicates the characterization and utilization of coal samples [3]. By studying the  
44 molecular structure of bituminous coal, its processing and utilization technology can be improved,  
45 thus improving coal classification and quality measure for use. Many researchers have studied the  
46 molecular structure of coal through various spectroscopic techniques, such as XRD [4-5], NMR [6],  
47 TEM [7], Raman [8-9] and FTIR [6,9] spectroscopy. However, due to the heterogeneity and complexity  
48 of coal, many problems and difficulties in the detailed characterization of its molecular structure  
49 remain. In this study, X-ray diffraction (XRD), Raman spectroscopy and Fourier Transform Infrared (FTIR)  
50 spectroscopy were used to investigate the molecular structure of coal.

51 X-ray diffraction [XRD] is a non-destructive technique that can obtain the molecular pattern of a  
52 sample. The diffraction angle/direction characterizes the shape and size of the unit cell, and the  
53 intensity reflects the arrangement of atoms in the unit cell [10]. By analyzing the diffraction pattern,  
54 the structural parameters such as aromaticity ( $f_a$ ), carbon stacking layer spacing ( $d_{002}$ ), average lateral  
55 sizes ( $L_a$ ), and stacking height of crystallite ( $L_c$ ) of the carbon accumulation structure can be calculated  
56 [11-12]. Since observation of the Raman Effect in 1928, Raman spectroscopy has been widely used in  
57 the characterization of carbonaceous materials, with techniques and analytical methods becoming  
58 more mature. The Raman spectrum of carbonaceous materials can be divided into first order and  
59 second order [13]. For graphite, there is only one band around  $1580\text{cm}^{-1}$ , which we called G band.  
60 While the study found that for highly disordered carbon, peak bands induced by micro-lattice defects  
61 appear at  $1150$ ,  $1350$ ,  $1530$  and  $1620\text{ cm}^{-1}$  in the first-order region [14-15]. And the intensity ratio of  
62 D1 and G band and the full width at half maximum (FWHM) of the G band has been proven to assess

63 the crystallinity and degree of order of the carbonaceous material [16-17]. Fourier transform infrared  
64 (FTIR) spectroscopy can be used to study and analyse the functional group composition of coal, and  
65 then to understand the molecular structure of coal [18-19]. This technology reveals the hydrocarbon  
66 structure including the aromatic and aliphatic, and heteroatomic functions (mainly oxygenated), and is  
67 one of the most powerful coal characterization technologies at present [20]. The data obtained by  
68 FTIR can calculate parameters such as  $f_a$ , (R/C) u, Hal/H and CH<sub>2</sub>/CH<sub>3</sub>, which can be used to  
69 quantitatively analyse the functional group composition and aromaticity of coal.

70 In summary, the reserves of bituminous coal account for a relatively large proportion in China, and  
71 its utilization still has great potential, but current research on the molecular structure of bituminous  
72 coal is incomplete because of our understanding of the heterogeneity and diversity of coal. Therefore,  
73 in this paper, XRD, Raman and FTIR spectroscopy techniques were applied to analyse the molecular  
74 structure of three groups of bituminous coal samples and a sub-bituminous coal sample which serve  
75 as comparative samples.

## 76 **2. Coal samples and experiment methods**

### 77 **2.1 Coal samples**

78 According to the large storage of bituminous coal in northern China, in this work, three bituminous  
79 samples were collected from coal mines of Daxing, Xiaoqing in Liaoning province and Xinyi in Henan  
80 province in China, which are coded as TFXQ, TFDX and YMX Y, respectively in this study. A comparative  
81 sub-bituminous coal sample is from coal mine Puhe in Liaoning province in China, which is marked as  
82 SBPH. These samples were demineralized before XRD, Raman and FTIR spectroscopy experiments,  
83 which can reduce the amount of minerals in order to improve the accuracy of quantitative analysis  
84 [21].

### 85 **2.2. Proximate and ultimate analysis**

86 Ultimate analysis was performed according to the international standard ISO 11722:2013 and ISO  
87 1171: 2010. Proximate analysis was carried out in accordance with ISO 17247: 2013 and ISO 19579:  
88 2006. The Ro was measured under polarized conditions by a microscope photometer (Zeiss, Germany)  
89 according to international standards ISO 7404-5:1984.

90 Parameters, such as the apparent aromaticity ( $f_a$ ), the ratio of aliphatic hydrogen (Hal) to total

91 hydrogen atoms (H)  $H_{al}/H$  and the number of the rings of aromatic carbon in the monomer  $(R/C)_u$ , can  
 92 be calculated from the data of proximate analysis and ultimate analysis. To characterize aromaticity,  
 93 Mielczarski et al. proposed  $f_a$  which can be calculated according to the Eq. (1).

$$94 \quad f_a = (100 - VM) \times 0.9677/C \quad (1)$$

95 where VM represents volatiles matter and C is the carbon content. 0.9677 is the fitting coefficient [22].  
 96  $(R/C)_u$  represents the number of rings of aromatic carbon in the monomer, which can be calculated  
 97 according to the Eq. (2) proposed by Kastner[23].

$$98 \quad (R/C)_u = 1 - \frac{f_a}{2} - \frac{(H/C)}{2} \quad (2)$$

99 where  $H_{al}/H$  represents the ratio between the concentrations of aliphatic ( $H_{al}$ ) and the total hydrogen  
 100 atoms (H), which can be calculated by Eq. (3)[24]:

$$101 \quad H_{al}/H = (1 - f_a)/(C_{al}/H_{al})/(H/C) \quad (3)$$

102 where  $C_{al}/H_{al}$  value is the atomic ratio between C and H in aliphatic groups, which is known to be  
 103 about 5.5 for coals.

### 104 **2.3. X-ray diffraction analysis**

105 The XRD experiment was performed by the D8 ADVANCE X-ray diffractometer manufactured by  
 106 Bruker, Germany and  $CuK\alpha$  radiation (40kV, 30mA). Detailed experimental conditions are as follows. Ni  
 107 fillers were used to filter out  $Cu-K\beta$  radiation. Besides, DS (Divergence Slit) and SS(Anti-scatter slit)  
 108 were 0.6mm and 8mm respectively. Detector opening was  $2.82^\circ$ , while Primary soller slit and  
 109 Secondary soller slit were both  $2.5^\circ$ . Powdered samples were scanned from  $3^\circ \sim 75^\circ$  in  $2\theta$  range with  
 110  $0.019450^\circ$  step interval and 0.2sec/step counter-time. Origin 2017 software was used to denote the  
 111 XRD spectrum. The broad hump was fitted to three Gaussian peaks around  $20^\circ$ ,  $26^\circ$  and  $42^\circ$ ,  
 112 representing  $\gamma$  peak, 002 peak and 100 peak respectively. The peak position ( $\theta$ ), intensity (I), area (A)  
 113 and full width at half maximum( $\beta$ ) were determined by XRD spectrum. The number of aromatic  
 114 carbon atoms ( $C_{ar}$ ) and aliphatic carbon atoms ( $C_{al}$ ) are equal to the areas under 002 peak and  $\gamma$  peak  
 115 respectively [9, 25, 26]. Therefore, the aromaticity( $f_a$ ) which is the ratio of carbon atoms in aromatic  
 116 rings, can be calculated by the Eq.(4)[4]:

$$117 \quad f_a = C_{ar}/(C_{ar} + C_{al}) = A_{002}/(A_{002} + A_\gamma) \quad (4)$$

118 where  $A_{002}$  and  $A_\gamma$  are the areas of the 002 peak and the  $\gamma$  peak, respectively. The lateral size ( $L_a$ ) which

119 provides the in-plane dimension of crystalline carbon and the staking height ( $L_c$ ) contributes the height  
120 of the crystalline carbon can be obtained by Debye-Scherrer Eqs.(5-6). The  $d_{002}$  can be calculated by  
121 Braggs Eq. (7).

$$122 \quad L_a = 1.84\lambda/(\beta_{002} \cos\theta_{002}) \quad (5)$$

$$123 \quad L_c = 0.89\lambda/(\beta_{100} \cos\theta_{100}) \quad (6)$$

$$124 \quad d_{002} = \frac{\lambda}{2\sin\theta_{002}} \quad (7)$$

125 where  $\lambda$  represents the wavelength of the X-ray( $\lambda=0.15405\text{nm}$ ),  $\beta_{002}$  and  $\beta_{100}$  are the FWHM (full width  
126 at half maximum) of the 002 peak and the 100 peak, respectively. The  $\theta_{002}$  and  $\theta_{100}$  are the diffraction  
127 angles corresponding to the peak positions of 002 peak and 100 peak.

#### 128 **2.4. Raman spectroscopy analysis**

129 Raman measurement was carried out to study the changes in the molecular structure, using a  
130 Senterra Raman spectrometer produced by Bruker, Germany at room temperature. The experiment  
131 was completed at the Modern Analysis and Computing Center of China University of Mining and  
132 Technology. Samples were demineralized and ground into powder (200 mesh) before measuring  
133 molecular parameters with a laser confocal Raman spectrometer. Equipped with a 532 nm laser, a  
134 laser power of 5 mW, a resolution of 9–18  $\text{cm}^{-1}$ , an integration time of 2 s, a cumulative number of 10  
135 times was used. The spectral resolution is less than or equal to 1.5  $\text{cm}^{-1}$ , lateral resolution is less than  
136 1 mm, longitudinal resolution is less than 2 mm, and the excitation wavelengths are 785 nm, 633 nm,  
137 and 532 nm, respectively. Applying Origin 2017 to fit Raman spectral peaks between 1000 and 2000  
138  $\text{cm}^{-1}$ . We obtained the intensity( $I$ ), peak position( $\theta$ ) and full width at half maximum (FWHM). The  
139 microcrystalline planar crystalline size  $L_a$  can be calculated by Eq.(8)[27]:

$$140 \quad L_a = C(\lambda_L)[I_D/I_G]^{-1} \quad (8)$$

141 where  $\lambda_L$  is the wavelength of Raman laser,  $C(\lambda_L)$  is the wavelength pre-factor,  $I_D$  and  $I_G$  are the  
142 intensity of the D and G bands respectively.  $C(\lambda_L)$ . This can be calculated by Eq. (9):

$$143 \quad C(\lambda_L) = C_0 + \lambda_L C_1 \quad (9)$$

144 where  $C_0=-12.6 \text{ nm}$ , and  $C_1=0.033$ .

#### 145 **2.5. FTIR spectroscopy analysis**

146 To study the molecular structure and its chemical bond it is necessary to use FTIR spectroscopy.

147 This determines the molecular bond length, infers the three-dimensional configuration of the  
 148 molecule, and determines the organic functional group composition in the sample. The FTIR  
 149 experiment was conducted at the Modern Analysis and Computing Center of China University of  
 150 Mining and Technology by a TIR Vertex 80v infrared spectrometer manufactured by Bruker, Germany.  
 151 The coal sample, which had been abraded into powder and demineralized, was scanned 32 times in  
 152 the wavenumber range of 4000–400 cm<sup>-1</sup> with a spectral resolution of 8 cm<sup>-1</sup>. Origin 2017 software  
 153 was used to fit the peaks of the spectrum map. Infrared spectrum fitting peaks provides key  
 154 information on the relative concentrations of aromatic carbons (C<sub>ar</sub>), aliphatic carbons (C<sub>al</sub>), and  
 155 carbonyl (C=O) groups etc. [28]. The apparent aromaticity (*f<sub>a</sub>*) can be calculated by Eq. (10-14):

$$156 \quad H_{ar} = \frac{A_{ar}}{a_{ar}} \quad (10)$$

$$157 \quad H_{al} = \frac{A_{al}}{a_{al}} \quad (11)$$

$$158 \quad \frac{H_{al}}{H} = \frac{H_{al}}{H_{al}+H_{ar}} = \frac{A_{2800-3000}}{A_{2800-3000}+A_{700-900}} \quad (12)$$

$$159 \quad \frac{C_{al}}{C} = \left( \frac{H_{al}}{H} \times \frac{H}{C} \right) / \frac{H_{al}}{C_{al}} \quad (13)$$

$$160 \quad f_a = 1 - \frac{C_{al}}{C} \quad (14)$$

161 where A<sub>ar</sub> and A<sub>al</sub> are the integral areas of absorbance in the aromatic hydrogen (900-700 cm<sup>-1</sup>) and  
 162 aliphatic hydrogen (3000-2700 cm<sup>-1</sup>) bands, respectively; a<sub>ar</sub> and a<sub>al</sub> (extinction coefficients) are used  
 163 to convert the integral area of absorbance to concentration content. For lignite and sub-bituminous  
 164 coal, the a<sub>ar</sub> is 541 cm<sup>-1</sup> and the a<sub>al</sub> is 710 cm<sup>-1</sup>. H<sub>al</sub>/H is the ratio between the concentrations of  
 165 aliphatic (H<sub>al</sub>) and the total hydrogen atoms (H), H<sub>ar</sub> is the aromatic hydrogen, H/C is the ratio of  
 166 hydrogen atoms to carbon atoms, calculated from the ultimate analysis, A<sub>2800-3000</sub> and A<sub>700-900</sub> are  
 167 integrated absorbance band areas at 2800–3000cm<sup>-1</sup> and 700-900cm<sup>-1</sup>. The aliphatic structural  
 168 parameter A(CH<sub>2</sub>)/A(CH<sub>3</sub>) is calculated by Eq. (15) [28]:

$$169 \quad \frac{A(CH_2)}{A(CH_3)} = \frac{A_{2935-2919}}{A_{2975-2950}} \quad (15)$$

### 170 3. Results and discussion

#### 171 3.1. Coal chemical properties of bituminous coal

172 According to Eqs.(1)-(3), the proximate and ultimate analyses results are shown in Table 1.  
 173 Industrial analysis (M, A, VM, FC) of these samples were performed according to GB/T 476-2008, GB/T

174 212-2008 and GB/T 483-87. The ranges of the parameters  $f_a$ ,  $(R/C)_u$ ,  $H_{ai}/H$  are 0.78-0.96, 0.49-0.57,  
 175 and 0.06-0.55, respectively.

176 Table 1 Proximate and ultimate analyses results

Sample	Proximate analysis (wt.%)				Ultimate analysis (wt.%)					H/C	$R_o$ (%)	$f_a$	$(R/C)_u$	$H_{ai}/H$
	M	A	VM	FC	C	H	O	N	S					
SBPH	15.12	19.12	42.50	23.26	71.49	5.23	17.53	4.05	0.49	0.88	0.43	0.78	0.57	0.55
TFXQ	8.43	36.09	28.04	27.44	68.18	4.98	15.35	2.03	0.47	0.88	0.57	0.93	0.50	0.17
TFDX	5.23	19.46	30.17	45.14	70.65	5.01	14.11	1.69	0.53	0.85	0.70	0.96	0.49	0.10
YMXY	3.03	5.98	20.67	72.32	90.04	4.05	7.33	1.37	2.88	0.54	1.09	0.85	0.55	0.06

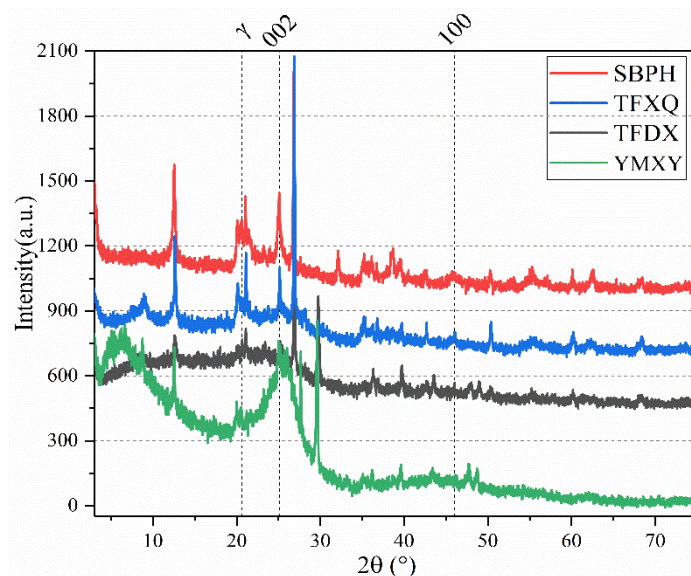
177 M: moisture; A: ash, on a dry basis; VM: volatile matter, on dry ash free (daf) basis; FC: fixed carbon (daf basis); all  
 178 ultimate analyses reported on a daf basis except sulfur on a dry basis;  $R_o$ : mean random vitrinite reflectance (%  
 179 oil).

180 It can be seen from the table that the results of the industrial analysis of the four coal samples are  
 181 quite different, the range of moisture (M) is 3.03~15.12%, the range of ash (A) is 5.98~36.09, the  
 182 range of volatile fraction (VM) is 20.67~42.50% and the range of fixed carbon (FC) is 23.26~72.32%,  
 183 among which the fixed carbon content of SBPH, TFDX and TFXQ samples is low, while the fixed carbon  
 184 content of the meager coal sample YMXY is significantly higher than other samples. Elemental analysis  
 185 of the four coal samples showed that the elemental content of the coal samples was dominated by C  
 186 elements, followed by O and H elements, with N and S elements accounting for a very small  
 187 proportion. The residual element content varies greatly between the coal samples, except for the H  
 188 element, which varies little. The content range of element C is 68.18~90.04%, H is 4.05~5.23%, O is  
 189 7.33~17.53, N is 1.37~4.05, S is 0.47~2.88%, and  $R_o$  is 0.43~1.09%. TFDX, TFXQ and YMXY belong to  
 190 bituminous coal (medium rank coal) while SBPH belongs to sub-bituminous coal (low rank coal),  
 191 according to the international standard ISO 11760:2005.

### 192 3.2. X-ray diffraction analysis

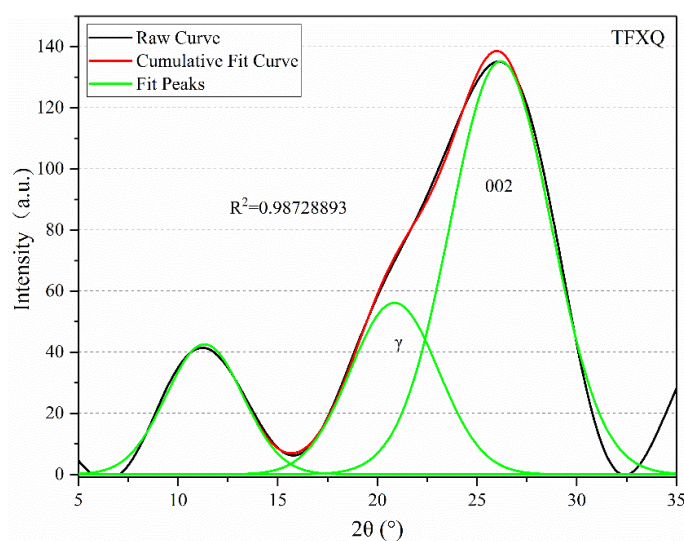
193 Fig. 1 shows the X-ray diffraction spectra of the four groups of coal samples used in the  
 194 experiment. It can be seen that each coal sample has basically the same characteristics and all show  
 195 high background intensity, which indicates that the coal sample contains a highly disordered material  
 196 with a definite proportion of amorphous carbon form. There are two clear peaks in the figure, and the  
 197 corresponding diffraction angles are located at about 26 ° and 47 °, respectively, which are 002 and  
 198 100 peaks. The 002 band shown in the figure relates to the stacking between the aromatic ring layers

199 which corresponds to the ordinary crystallites formed by poly-condensation of the aromatic core, i.e.  
 200 the aromatic crystallites. The  $\gamma$  band which located at the left side of the 002 peak is caused by  
 201 aliphatic hydrocarbon branches, various functional groups, and alicyclic hydrocarbons, called branched  
 202 crystallites, which are connected to the poly-condensation aromatic core.



203  
 204 Fig. 1 The XRD spectra of four coal samples

205 Due to the stacking of peaks, we used Origin 2017 to perform split-peak fitting of peaks from 5° to  
 206 35°, resulting in two Gaussian peaks, 002 and  $\gamma$ , which were fitted near 20° and 26°, respectively, to  
 207 obtain information on the corresponding parameters such as peak position, area, half-height and  
 208 width. Fig. 2 shows the fitting curve of the TFXQ coal sample at 5 to 35°.



209  
 210 Fig. 2 Gaussian fitting curve of  $\gamma$  peak and 002 peak of TFXQ coal sample in  $2\theta$  range of 5-35°  
 211 From the results of peak fitting, we can obtain the area of the 002 peak and  $\gamma$  peak, and thus the

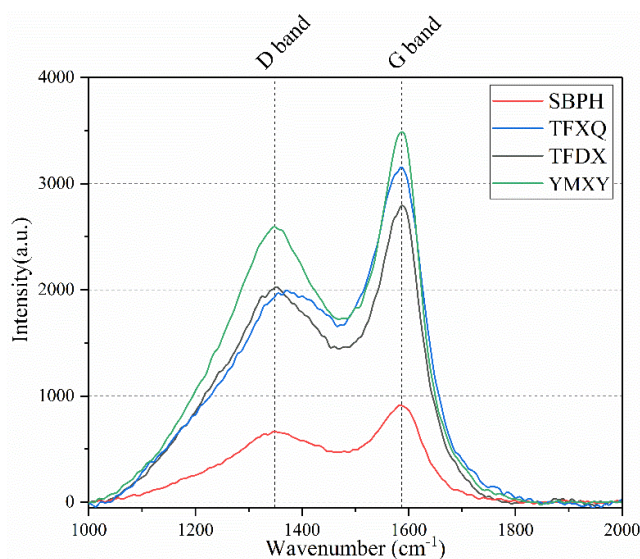
212 sample parameters  $d_{002}$ ,  $f_a$ ,  $L_c$  and  $L_a$  can be calculated using Eqs. ((4)-(7)). The results are shown in  
 213 Table 2. The range of  $d_{002}$  can be found to be 3.40 to 3.52 Å, indicating that the coal samples contains  
 214 a low degree of ordered microcrystalline units relative to pure graphite (3.36 to 3.37 Å). The range of  
 215 parameter aromaticity  $f_a$  is 0.62 to 0.91.  $L_c$  and  $L_a$  reflects both the lamellar ductility and stacking of  
 216 the microcrystals with values ranging from 17.27 to 25.88 Å and 25.78 to 27.93 Å, respectively. The  
 217 aromatization of bituminous coal is not generally high. The TFXQ and YMXV coals have higher  
 218 aromaticity  $f_a$  among the four samples, and their  $L_a$  and  $L_c$  values are relatively large. This also implies  
 219 that the microcrystalline size is correspondingly larger for the more aromatized coal samples, which  
 220 also implies greater microcrystalline ductility and stacking. The bituminous coal samples in this study  
 221 contain a low degree of ordered microcrystalline units with a low degree of aromatic conformation.

222 Table 2 XRD structure parameters

Sample	$d_{002}$ (Å)	$f_a$	$L_c$ (Å)	$L_a$ (Å)
SBPH	3.52	0.69	20.51	26.61
TFXQ	3.40	0.73	25.88	27.93
TFDX	3.42	0.62	17.27	25.78
YMXV	3.49	0.91	23.33	26.49

### 223 3.3 Raman spectroscopy analysis

224 Fig. 3 shows the Raman spectrum of the first-order mode range (1000-2000  $\text{cm}^{-1}$ ) after baseline  
 225 correction.



226

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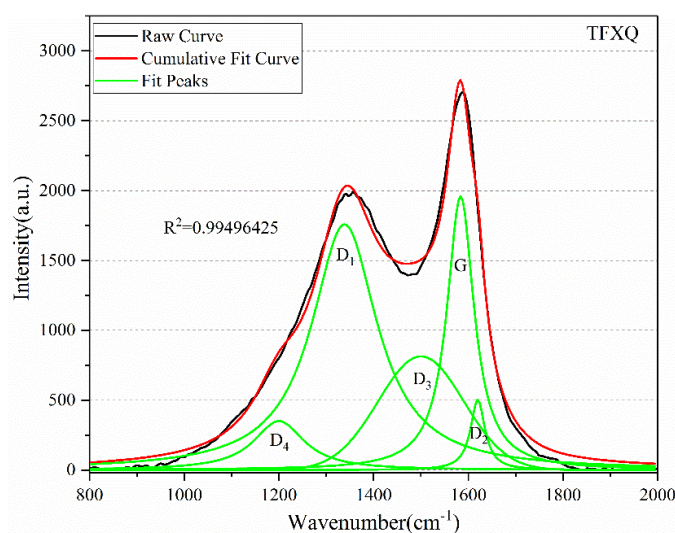
229

Fig. 3 The Raman spectra of four coal samples

Two distinct Raman frequency vibration regions can be clearly seen, that is, D band located near  
 1350  $\text{cm}^{-1}$  and G band near 1590  $\text{cm}^{-1}$ . Due to the overlap between D and G bands, the use of only D

230 and G bands in Raman spectroscopy will result in the loss or neglect of information about the  
231 properties of highly disordered carbonaceous materials [29]. Therefore, further integration of the  
232 Raman spectrum of the coal (peak fitting) is needed to obtain the hidden information of the skeleton  
233 carbon structure in the overlapping region. The method of Sadezky et al. [30] was used to solve this  
234 problem.

235 Take the TFXQ sample as an example, the Raman spectrum data obtained from the experiment  
236 was smoothed and the peak fitting was performed firstly. It was found in the result that the  
237 combination of four Lorentz peaks ( $D_1$ ,  $D_2$ ,  $D_4$ , G) located near  $1360$ ,  $1620$ ,  $1180$ , and  $1580\text{cm}^{-1}$  and a  
238 Gaussian peak ( $D_3$ ) near  $1500\text{cm}^{-1}$  were the most suitable and the fitting result is shown in Fig. 4.  
239 Based on the findings related to natural graphite and Raman spectra this show the carbonaceous  
240 material, a carbon atom with double stretching vibration peaking at G. This relates to the molecular  
241 structure, with vibration attributable to the aromatic  $E_{2g2}$  plane.  $D_1$  relates to C-C bond peak vibrations  
242 between the aromatic ring and at least a 6 ring aromatic compound. The mode of vibration is  
243 attributable to the amorphous graphite  $A_{1g}$  irregular hexagonal lattice structure, defect intermolecular  
244 structural units and Heteroatom-related [30-33].



245  
246 Fig. 4 Raman spectrum of TFXQ coal with the corresponding curve fitted bands  
247 Positions of G peak and  $D_1$  peak, difference of peak position (G- $D_1$ ), and integrated intensity ratio  
248 ( $I_{D1}/I_G$ ) and other characteristic parameters are important parameters for evaluating the degree of  
249 crystallinity or degree of defects in carbonaceous materials. The output data is shown in Table 3. It can  
250 be seen from Table 3 that the peak positions of the G and  $D_1$  peaks of the four coal samples are

251 relatively close, and they are distributed near  $1583\text{ cm}^{-1}$  and  $1335\text{ cm}^{-1}$ , which indicates that the  
 252 ordered structures in the four coal samples were similar. The range of G-D<sub>1</sub> is  $245.06 - 249.63\text{ cm}^{-1}$ . Its  
 253 value of G-D<sub>1</sub> is higher than that of anthracite [42]. The peak position difference of the SBPH coal  
 254 sample is the largest of the four, indicating that the coal sample has less disordered structure than  
 255 other coal samples [34]. The range of I<sub>D1</sub> / I<sub>G</sub> is  $2.18 \sim 2.48$ , among which the value of SBPH coal is  
 256 significantly larger, indicating that its degree of graphitization is the lowest. On the contrary, the TFXQ  
 257 coal sample has a better graphitization structure [16]. It is reported that as the coal metamorphism  
 258 temperature increases, the G zone becomes the main zone, and the D zone gradually disappears,  
 259 indicating that the structure of anthracite contact metamorphic coal is close to well-crystallized  
 260 graphite [35]. The value of I<sub>D1</sub> / I<sub>G</sub> for bituminous coal is higher than that for anthracite [42], which also  
 261 means that bituminous coal is less graphitized than anthracite. Therefore, bituminous coal has a lower  
 262 combustion calorific value than anthracite, and has few advantages in combustion applications. The  
 263 value of  $L_a$  ranges from 18.16 to 20.64, which is lower than the value calculated by XRD.

264 Table 3 Peak fitting parameters of Raman spectra of four coal samples

Sample	Peak	Position( $\text{cm}^{-1}$ )	Intensity	FWHM	G-D <sub>1</sub>	I <sub>D1</sub> /I <sub>G</sub>	$L_a$ (Å)
SBPH	G	1582.99	102800.00	69.46	249.63	2.48	18.16
	D <sub>1</sub>	1333.36	254500.00	177.78			
TFXQ	G	1583.65	21400.00	69.42	245.06	2.18	20.64
	D <sub>1</sub>	1338.59	466200.00	168.66			
TFDX	G	1583.62	120700.00	70.51	248.45	2.31	19.43
	D <sub>1</sub>	1335.16	279300.00	180.83			
YMX Y	G	1583.24	237700.00	69.66	247.82	2.37	18.95
	D <sub>1</sub>	1335.42	564000.00	175.55			

### 265 3.4 FTIR spectra analysis

266 The FTIR spectra of the four groups of coal samples are shown in Figure 5.

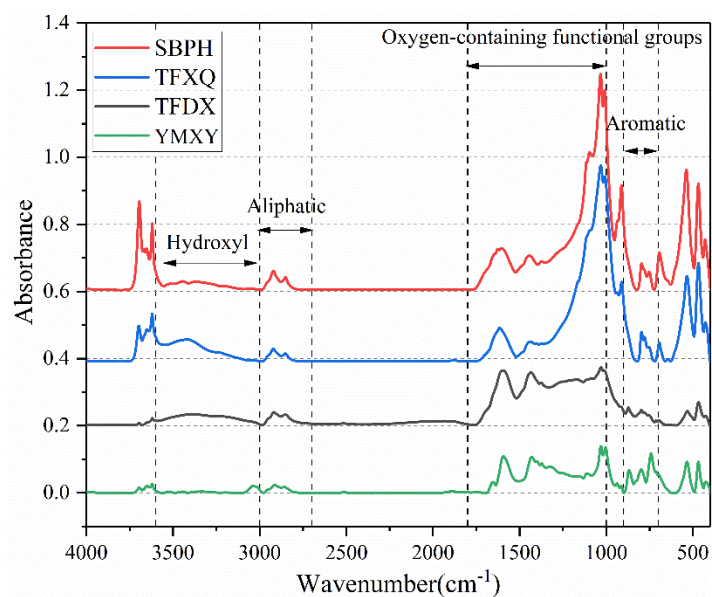


Fig.5 FTIR spectra of four coal samples

267

268

269 According to prior research, the main functional groups of coal include hydroxyl, aromatic,  
 270 aliphatic and oxygen-containing functional groups. Their approximate range is shown in Figure 5. The  
 271 hydroxyl and aliphatic absorption peak, the oxygen-containing functional group absorption peak and  
 272 the aromatic structure absorption peak are located at 3600~3000 cm<sup>-1</sup>, 3000~2700 cm<sup>-1</sup>, 1800~1000  
 273 cm<sup>-1</sup> and 900~700 cm<sup>-1</sup> in the FTIR spectra, respectively. Specific peaks corresponding to the functional  
 274 group are listed in Table 4.

275 Table 4 Corresponding assignment table of characteristic peaks of FTIR spectra [36-38]

Number	Peak position	Wavenumber range	Functional group assignment
1	3680	3685-3600	free -OH
2	3550	3600-3500	-OH self-contained hydrogen bond
3	3400	3550-3200	-OH stretching vibration
4	2950	2975-2950	CH <sub>3</sub> asymmetric stretching vibration
5	2920	2935-2915	CH <sub>2</sub> asymmetric stretching vibration
6	2870	2875-2860	CH <sub>3</sub> symmetric stretching vibration
7	2850	2860-2840	CH <sub>2</sub> symmetric stretching vibration
8	1750	1770-1800	Aliphatic C = O stretching vibration
9	1700	1715-1690	Aromatic C = O stretching vibration
10	1675	1690-1660	C = O stretching vibration in quinone
11	1600	1605-1595	Aromatic C = C stretching vibration
12	1470	1480-1465	CH <sub>2</sub> asymmetric deformation vibration
13	1440	1460-1435	CH <sub>3</sub> asymmetric deformation vibration
14	1380	1385-1370	CH <sub>3</sub> symmetric bending vibration
15	1150	1160-1120	C-O-C stretching vibration
16	1110	1120-1080	S = O stretching vibration

17	1050	1060-1020	Si-O-Si or Si-O-C stretching vibration
18	870	900-850	aromatic nucleus (CH), one adjacent H deformation
19	820	825-800	aromatic nucleus (CH), three adjacent H deformation
20	750	770-730	aromatic nucleus (CH), five adjacent H deformation
21	720	724-716	n-Alkane side chain skeleton (CH <sub>2</sub> ) <sub>n</sub> oscillatory vibration

### 276 3.3.1 Qualitative analysis

277 Due to the condition of multiple peaks superimposed in the original image, the image needs to be  
 278 deconvolved by Origin2017 to fit the specific functional group absorption peak information. By fitting  
 279 the peaks in different regions, we can obtain information on different kinds of functional groups. The  
 280 absorption peaks in the range of 3700-3000 cm<sup>-1</sup> are predominantly hydroxyl. The absorption peaks of  
 281 the samples are concentrated in the 3700-3600 cm<sup>-1</sup> range, so there is a lot of free OH, which in turn  
 282 can be judged to be likely to contain alcohols, phenols and organic acids [36]. The absorption peaks in  
 283 the range of 3000-2700 cm<sup>-1</sup> are aliphatic structures. Significant absorption peaks can be seen to be  
 284 fitted at the peaks at 2950, 2920, 2870, 2850 cm<sup>-1</sup>, and they correspond to the CH<sub>3</sub> asymmetric  
 285 stretching vibration, CH<sub>2</sub> asymmetric stretching vibration, CH<sub>3</sub> symmetric stretching vibration and CH<sub>2</sub>  
 286 symmetric stretching vibration, respectively.

#### 287 3.3.1.1 Fitting analysis of 1800-1000cm<sup>-1</sup> area

288 FTIR fitting curves for the absorption peaks in the range of 1800-1000 cm<sup>-1</sup> for SBPH and YMX  
 289 coal samples are shown in Figure 6. Most of the absorption peaks in this range are oxygen-containing  
 290 functional groups. The absorption peaks of the three groups of bituminous coal samples, were similar  
 291 in shape, with larger absorption in the 1100-1000 cm<sup>-1</sup> range and somewhat sharp shapes. This  
 292 indicates the presence of more S=O telescopic vibrations, Si-O-Si or Si-O-C telescopic vibrations.  
 293 Moreover, the four sets of samples showed significant peaks at 1600 and 1440 cm<sup>-1</sup>, so that the  
 294 presence of aromatic C=C stretching vibrations and CH<sub>3</sub> asymmetric deformation vibrations could be  
 295 judged. A smaller absorption peak at 1700 cm<sup>-1</sup>, a C=O stretching vibration in the aromatics, was also  
 296 observed by fitting the curve.

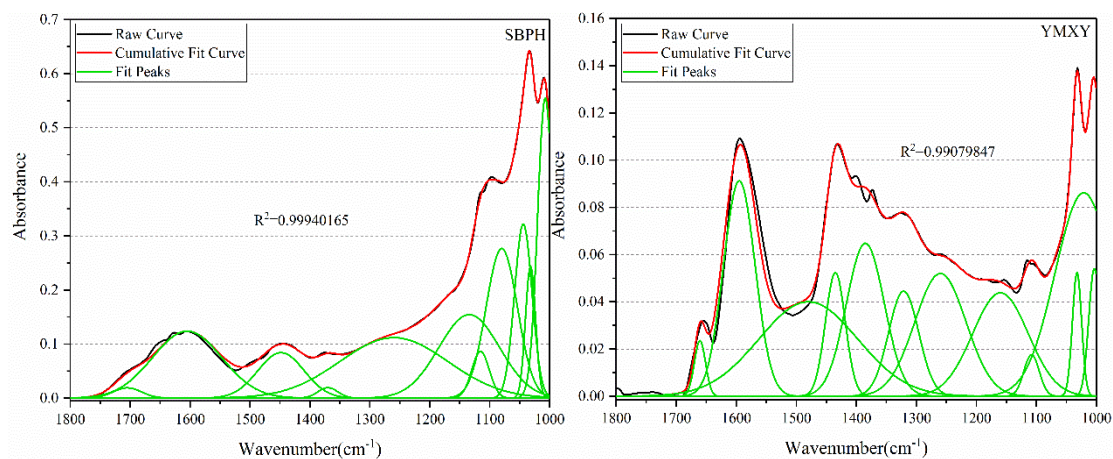


Fig. 6. 1800–1000  $\text{cm}^{-1}$  FTIR spectra fitting curve of SBPH and YMXY

### 3.3.1.2 Fitting analysis of 900-700 $\text{cm}^{-1}$ area

FTIR fitting curves for the absorption peaks in the range of 900-700  $\text{cm}^{-1}$  for SBPH and YMXY coal samples are shown in Figure 7. The absorption area in the wavenumber range of 900-700  $\text{cm}^{-1}$  is mainly formed by the bending vibrations of poly-substituted aromatics. The absorption peaks of the SBPH coal sample is concentrated in the 900-800 $\text{cm}^{-1}$  wavelength range, suggesting that it contains mainly benzene ring structures in which individual H atoms are replaced by CH. While the absorption peaks of YMXY sample, is more uniformly distributed in the 900-700  $\text{cm}^{-1}$  wavelength range, reflecting the benzene ring structure with a single H atom, three adjacent H atoms and five adjacent H atoms replaced by CH, and the n-alkane side chain backbone ( $\text{CH}_2$ ) structure.

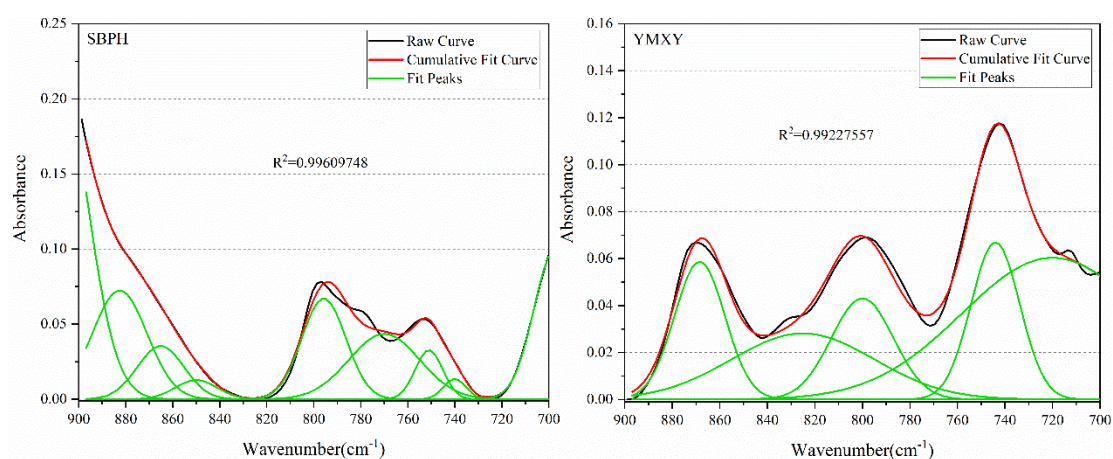


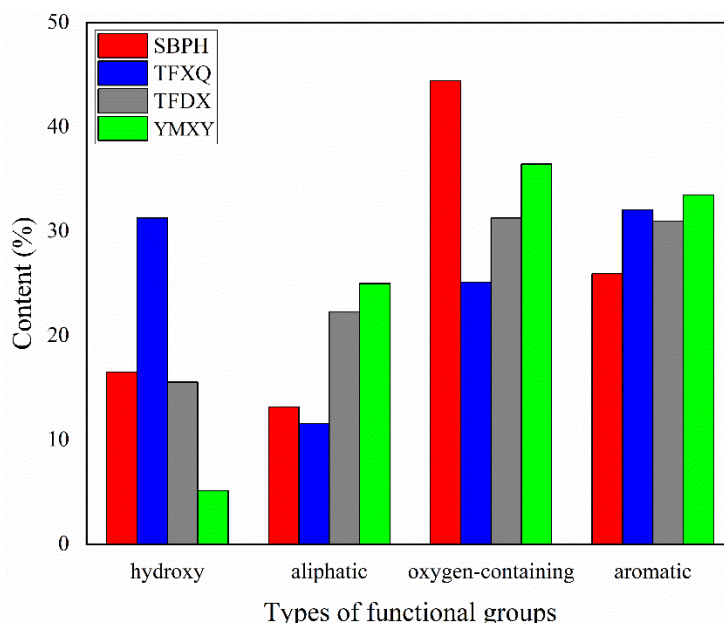
Fig. 7 900–700  $\text{cm}^{-1}$  FTIR spectra fitting curve of SBPH and YMXY

310 **3.3.2 Quantitative analysis**

311 After determining the functional group, the area of its absorption peak can be obtained, and then  
 312 the parameters of aromaticity  $f_a$ ,  $(R/C)_u$  and  $CH_2/CH_3$  can be calculated by Eqs.(10-15). Areas of  
 313 absorption peaks of major functional groups in FTIR spectra are shown in Table 5. The proportion of  
 314 hydroxyl groups, aliphatic groups, oxygenated functional groups and aromatic groups can be obtained  
 315 by area normalization and the results are shown in Figure 8. It can be seen from the figure that the  
 316 commonality of the three groups of bituminous coal (medium rank coal) samples is a large proportion  
 317 of oxygen-containing functional groups and aromatic groups but lower than those of anthracite [42].  
 318 In addition, the hydroxyl content of bituminous coal (medium rank coal) is also higher than that of  
 319 anthracite. Most of the oxygen-containing functional groups are hydrophilic groups that are easy to  
 320 combine with hydrophilic substances, thereby forming composite materials with other impurities in  
 321 bituminous coal, so they may be made into filters to treat wastewater [39].

322 Table 5 Area of absorption peaks of major functional groups in FTIR spectra

Sample	Hydroxyl groups	Aliphatic groups	Oxygen-containing functional groups	Aromatic groups
SBPH	17.12	13.67	46.12	26.91
TFXQ	23.98	8.87	19.25	24.58
TFDX	14.06	20.16	38.32	28.05
YMXY	1.96	9.60	14.00	12.86



323

324 Fig.8 Proportion of different functional groups

325 Based on a simple understanding of the functional group occupancy, aromatic  $f_a$ , lipid hydrogen

326 ratio Hal/H, single carbon ring number (R/C)<sub>u</sub> and aliphatic structural parameter CH<sub>2</sub>/CH<sub>3</sub> can be  
327 obtained by Eqs. (10-15). The results are shown in Table 6.

328 Table 6 Molecular structure parameters of four bituminous coal samples obtained by FTIR method

Sample	H/C	Hal/H	Cal/C	$f_a$	(R/C) <sub>u</sub>	A(CH <sub>2</sub> )/A(CH <sub>3</sub> )
SBPH	0.88	0.60	0.29	0.71	0.21	0.32
TFXQ	0.88	0.34	0.17	0.83	0.14	0.18
TFDX	0.85	0.72	0.34	0.66	0.25	0.13
YMXY	0.54	0.52	0.16	0.84	0.31	0.13

329 Among them,  $f_a$  and (R/C)<sub>u</sub> reflect the information of aromatic structure in the macromolecular  
330 structure of coal to a certain extent, so as to judge the degree of aromatization of coal. CH<sub>2</sub>/CH<sub>3</sub>  
331 reflects the length of aliphatic side chains in coal [37-38]. These parameters are an important basis for  
332 analysing the influence of coal molecular structure on its physical properties. It can be seen from Table  
333 6 that the  $f_a$  of two coal samples of TFXQ and YMXY is larger than that of the other two coal samples,  
334 indicating that these two coal samples have a higher degree of aromatization [40-41]. However,  
335 although the  $f_a$  of the TFXQ coal sample is relatively large, its single carbon ring number (R/C)<sub>u</sub> is  
336 relatively small. Contrary to  $f_a$ , Hal/H reflects the higher content of aliphatic structure in the two coal  
337 samples of TFDX and SBPH than the other two coal samples. CH<sub>2</sub>/CH<sub>3</sub> reflects that SBPH coal-like  
338 macromolecules have longer aliphatic side chains. Comparing the parameters of these three groups of  
339 bituminous coal samples with the anthracite samples [42], we can find that their  $f_a$  is lower than that  
340 of the anthracite, so the bituminous coal has a lower degree of aromatization than anthracite. In  
341 addition, its CH<sub>2</sub>/CH<sub>3</sub> value is lower than that of high rank coal, so the aliphatic side chains of  
342 bituminous coal are shorter.

#### 343 4. Conclusions

344 In this study, the molecular structure of bituminous coal and sub-bituminous coal was investigated  
345 using three methods, X-ray diffraction, Raman spectroscopy and Fourier Transform Infrared  
346 spectroscopy. From the qualitative and quantitative analysis of industrial analysis and spectroscopic  
347 test results, the conclusions are as follows:

348 (1) The results of industrial analysis show that the water content of different coal samples varied  
349 greatly, with the values ranging from 3.03 to 15.12%. The results of elemental analysis show that the

350 elemental content of bituminous coal was dominated by C elements, followed by O and H elements,  
351 with N and S elements accounting for a very small proportion.

352 (2) The results of the XRD analysis suggest that the bituminous coal samples in this study contain a  
353 low degree of ordered microcrystalline units with a low degree of aromatic conformation.

354 (3) The analysis of the Raman spectroscopy results shows that the peak difference G-D<sub>1</sub> is the  
355 largest in the SBPH coal sample (sub-bituminous coal), indicating that the disordered structure is less  
356 in this sample than in other bituminous coal samples. And generally bituminous coal has less  
357 disordered structure than anthracite. The I<sub>D1</sub>/I<sub>G</sub> of the TFXQ coal samples are significantly smaller,  
358 indicating that the degree of graphitization is higher. The value of I<sub>D1</sub>/I<sub>G</sub> for bituminous coal is higher  
359 than for high rank coal, which means that medium rank coal is less graphitized than high rank coal.  
360 Therefore, bituminous coal has a lower combustion calorific value than anthracite, and has few  
361 advantages in combustion applications.

362 (4) FTIR experimental analysis shows that the absorption peak areas of the oxygen-containing  
363 functional groups in the samples are generally the largest, followed by the aromatic structure, the  
364 aliphatic structure and the hydroxyl functional group with relatively small absorption peak areas. In  
365 addition, the molecular structure parameters obtained from the analysis indicate that the YMX<sub>Y</sub> coal  
366 sample has a high degree of aromatization. The bituminous coal samples have a high content of  
367 aliphatic structure, and the SBPH coal sample has a long aliphatic side chain in the macromolecule.  
368 Parameter  $f_a$  of the bituminous coal is lower than that of the anthracite, so it has a lower degree of  
369 aromatization. Due to the large amount of oxygen-containing functional groups in bituminous coal, it  
370 has high hydrophilicity and can be used for adsorption and filtration

#### 371 **Notes**

372 The authors declare that we do not have any commercial or associative interest that represents a  
373 conflict of interest in connection with the work submitted.

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378 **Nomenclature**

379	$f_a$	the ratio of aromatic carbon to total carbon
380	$d_{002}$	inter-layer spacing (Å)
381	$L_a$	the average diameter of coal crystallites (Å)
382	$L_c$	the average height of coal crystallites (Å)
383	$\varphi$	peak position of XRD spectra (°)
384	$\lambda$	X-ray wavelength (Å)
385	$\lambda_L$	the wavelength of Raman laser (Å)
386	$\theta$	the diffraction angle of X-ray (°)
387	$C_{al}/H_{al}$	the atomic ratio between C and H in aliphatic groups
388	$C_{al}/C$	the aliphatic carbon fraction
389	$(R/C)_u$	the number of rings of aromatic carbon in the monomer
390	$H_{al}/H$	the ratio of aliphatic ( $H_{al}$ ) to the total hydrogen atoms (H)
391	$A(CH_2)/A(CH_3)$	the length of aliphatic chains or the degree of branching aliphatic side-chains

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### **Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# Molecular structure characterization of bituminous coal in Northern China via XRD, Raman and FTIR spectroscopy

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