

Optical and conductive properties of functional materials extracted from coal tar pitches treated by air oxidation method¹

Yan Zhan^a, Yan Song^a, Yue Zhan^a, Yimin^a,
Ainan An^a, Yongbin^b, Yinan^a, Yimin^a,
and Fei Zhou^{a*}

^a Key Laboratory of Advanced Coal and Coking Technology of Liaoning Province,
School of Chemical Engineering, University of Science and Technology Liaoning,
Anshan 114051, P. R. China

^b School of Materials and Metallurgy, University of Science and Technology Liaoning,
Anshan 114051, P. R. China

*e-mail: aszhou15242870697@163.com

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Abstract—The oligomers having the blue photoluminescence and conductivities of 5×10^{-7} – $7.4 \times 10^{-4} \text{ S m}^{-1}$ after doping by iodine are extracted successfully from coal tar pitches which were dealt with by the air oxidation method at 350°C. Meanwhile, it is observed that extracted materials have the blue photoluminescence with the fluorescence quantum yield of 7–10.2%. In these cases, we used the solutions of toluene and pyridine to extract these functional materials from coal tar pitches. Consequently, we consider these extracted materials showing the advantages in the application of fabricating the electronic devices, because it can decrease the production cost remarkably than use of the materials obtained by general organic synthesis methods. Finally, this research also can provide the one of beneficial references for solving the serious problem of overproduction of coal tar pitches in China. The oligomers having the blue photoluminescence and conductivities of 5×10^{-7} – $7.4 \times 10^{-4} \text{ S m}^{-1}$ after doping by iodine are extracted successfully from coal tar pitches which were dealt with by the air oxidation method at 350°C. Meanwhile, it is observed that extracted materials have the blue photoluminescence with the fluorescence quantum yield of 7–10.2%. In these cases, we used the solutions of toluene and pyridine to extract these functional materials from coal tar pitches. Consequently, we consider these extracted materials showing the advantages in the application of fabricating the electronic devices, because it can decrease the production cost remarkably than use of the materials obtained by general organic synthesis methods. Finally, this research also can provide the one of beneficial references for solving the serious problem of overproduction of coal tar pitches in China.

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INTRODUCTION

It is acknowledged that great mass of coal tar pitches are produced during the production of cokes made from coal. However, coal tar pitches with low additional value are usually applied in the fields such as paving the way and being used as binding agents. The researches about pitches have been started from the early 1960s [1, 2].

After Mochida et al. had pointed out that the existence of mesocarbon microbeads (MCMBs) when the coal tar pitches were coped by the two methods, such as the air oxidation method and heating under nitrogen gas, some groups make effort to study the MCMBs to increase the additional value of coal tar pitches in the world [3–11]. For instance, MCMBs made from coal tar pitches are expected to fabricate electrode materials of lithium-ion battery [12].

¹ The text was submitted by the authors in English.

Table 1. The characteristic properties of coal tar pitches from Ansteel Group Corporation

Characteristic ^a	Coal tar pitch
TI%	19.1
QI%	9.3
Softening point, °C	83.5
Water%	0.3
Ash%	0.2

^a TI is the toluene-insoluble part. QI is the quinoline-insoluble part.

In the past twenty years, with the development of organic light emitting diode (OLED) and organic field-effect transistor (OFET), the π -conjugated polymers have been attracted than ever before, for they have the advantages, such as good film-forming properties, and the electric charge recombination being able to realize in the inner-films, and so on [13–19]. However, the synthesizing of π -conjugated polymers is really difficult, and production cost of polymers is higher than the lower molecular weight molecules. These disadvantages influence the application of π -conjugated polymers in the field of the fabricating devices.

On the other hand, the air oxidization method has just provided the possibility for the polycondensation of polycyclic aromatic hydrocarbons (PAHs) with π -conjugated properties [20–23]. In the meantime, Afanansov et al. used the solvents to extract the organic materials from coal tar pitches and investigated the properties of them [24]. Based on these backgrounds, we attempt to obtain the π -conjugated materials from coal tar pitches because of their very low cost. As a consequence, in our study, we carried out the polycondensation of coal tar pitches via the air oxidization method, and extracted the parts of them in use of solvents of toluene and pyridines, respectively. The optical properties of extracted parts are evaluated by the photoluminescence measurements. The higher blue photoluminescence of 10.2% is observed by measurement of fluorescence spectrophotometer. Moreover, we use the doping method to dope the extracted materials by iodine. As a result, the relative high conductivity of $7.4 \times 10^{-4} \text{ S m}^{-1}$ of doped materials is observed. Especially, the conductive result shows the extracted materials have obvious semiconducting properties, enabling them to be applied in the field of fabricating the hole injection layer of OLED materials as they can decrease the drive voltage and extend the service life of devices.

EXPERIMENTAL

Measurements. The FTIR was determined on the instrument from Nicolet Company in America. The fluorescence properties were evaluated by the fluorescence detector (LS55) made in America. The molecular weight is measured by the GPC (Gel Permeation Chromatography) Cell Unit made in America. The UV-vis result is evaluated by the LAMBDA900 which is made in America. Pitch Softening Point is measured by the Pitch Softening Point Tester which was obtained from the LanTian Instrument, Co. Ltd, China.

Materials. Quinoline was purchased from DongXing Chemical Reagent, Shenyang, China. Toluene was purchased from Second Chemical Reagent, Shenyang, China. Pyridine and chloroform solvents were purchased from Sinopharm Chemical Reagent Co., Ltd, China. Fluorescein is purchased from Sinopharm Chemical Reagent Co., Ltd, which is used to evaluate the photoluminescence properties of extracted materials. Coal tar pitches were obtained from Ansteel Group Corporation Co., Ltd, China. The properties of coal tar pitches are evaluated, according to the CIS (Chinese Industrial Standards), which are shown in (Table 1).

Polymers condensations in coal tar pitches via the air oxidization method. Firstly, the solid coal tar pitches were ground to the particles, which were smaller than 3 mm in size. These pitch particles (300 g) were added into the reaction kettle (700 mL). It increased the reactive temperature to the 350°C, and the reactive cases were stirred with rotation rate of 180 rpm under air bubbling (45 L min^{-1}) for different heating times of 30 min and 60 min.

Preparation process of extracted polymers using iodine. We prepared the solutions of ethanol containing the iodine with weight ratio of 1, 5, and 7%, respectively. After adding the extracted oligomers into the prepared ethanol solutions and stirring the obtained mixtures for 24 h, the filtrates are obtained by the filtration and dried completely. As a result, the objective solid materials doped by iodine are obtained.

RESULTS AND DISCUSSION

Considering the actual productive cost, we use the general-purpose solvents such as toluene and pyridine to extract functional materials of coal tar pitches dealt with by air oxidization method at 350°C. Meanwhile, associating

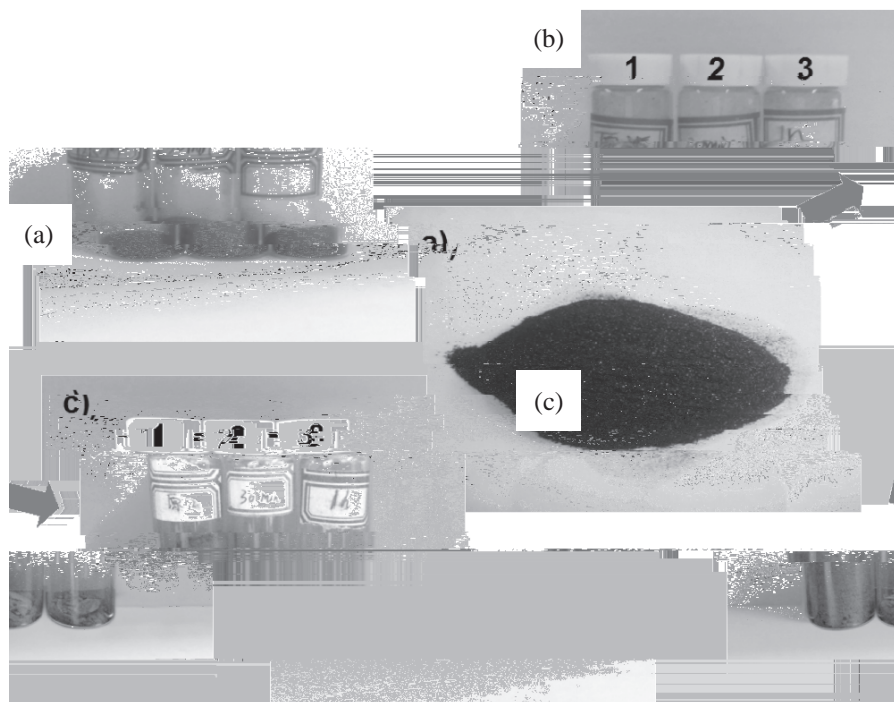


Fig. 1. The images of coal tar pitches (a) extracted parts obtained by (b) extraction in use of toluene solvent and (c) by extraction using pyridine solvent. The numbers of 1, 2 and 3 are the objective extraction coal tar pitches without any heating process and heated for the different heating time of 30 min and 60 min, respectively.

with the solubility of extracted parts, it carried out the air oxidization reaction for the short time of 30 min and 60 min, respectively. According to the Soxhlet extraction method, the heated coal tar pitches (2 g) are extracted by the solvents of toluene and pyridine, respectively. The extracted solvents are dealt with through the separating funnel using the water and chloroform solvents. The obtained chloroform solution is filtered by the thin layer of the silica gel so as to remove some black inorganic parts in the extracted materials. Finally, the filtrate was concentrated and the obtained solid was dissolved in the chloroform solution and purified by the general reprecipitation method using the *n*-hexane solvent. As a result, figures 1b and 1c show that the obtained deep brown solid are extracted from coal tar pitches which are heated for different time of 30 and 60 min under air flowing.

The evaluations of extraction effects by use of different solutions are illustrated in Table 2. Based on the fact that molecular weight showed the range of 452–929, the obtained extractive materials should be considered to be dimer, trimer and oligomers approximately. In addition, the extracted yield and molecular weight of extracted

parts in Fig. 1c are higher naturally than those in Fig. 1b, which causes the solubility of heated coal tar pitches in pyridine is higher than that in the toluene solvent. Especially, the oligomers having molecular weight around at 929 can be extracted by pyridine solvent with the yield of 14%. These results also should be considered that the extractive capabilities of toluene and pyridine solvents for heated coal tar pitches are limited, because the aromatic structures decrease the solubility of obtained materials in solvents of toluene and pyridine.

The UV-vis and PL results of extracted parts obtained from heated coal tar pitches are illustrated in Fig. 2. Considering the complexity of structures of extracted materials, we have to adjust the measurement solutions containing extracted materials by weight concentration to be used to evaluate the photoluminescence properties. Based on the general methods, we used the λ_{\max} absorption of UV-vis spectra as photoluminescence excitation wavelength to investigate photoluminescence properties. As shown in Fig. 2a, the λ_{\max} of a_2 and a_3 did not show the read shift obviously, comparing with the a_1 ($\lambda_{\max} = 260$ nm). However, compared with the absorptions top (λ_{\max}) in the same UV-vis curves, the absorptions intensity of shoulder peaks of a_2 and a_3 at

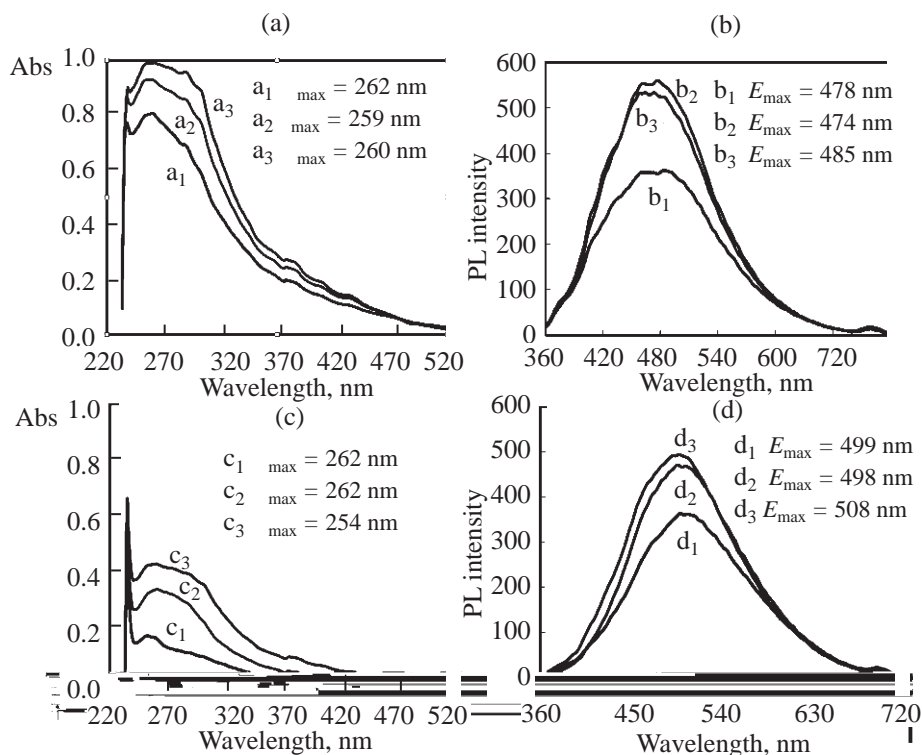


Figure 2. The UV-vis (a, c) and photoluminescence (PL) (b, d) results of extracted parts of coal tar pitches with and without heating process. The (a) and (b) are the extracted parts obtained by the toluene solvent dissolved in the chloroform with the same weight concentration of 0.5×10^{-5} wt %; (c) and (d) are the extracted parts obtained by the extraction solvent of pyridine dissolved in the chloroform solvent with the same weight concentration at 0.5×10^{-5} wt%. Among them, the numbers of 1, 2, and 3 are the objective extraction coal tar pitches without heating and heated for the different heating time of 30 min and 60 min, respectively.

289 and 290 nm are becoming stronger than the shoulder peak absorption of a₁ at 288 nm. Generally, when the air oxidation temperature was increased to the 350°C, the polycondensation among the aromatic rings by the bonding type of $-Ar-Ar-$ exists in the heated coal tar pitches [25]. However, in the toluene extracted parts, the polymerization degree of $-Ar-Ar-$ is really low, similar

to the dimer and trimer, because the toluene solvent only dissolved the parts having the low molecular weight in the heated coal tar pitches (Table 2). On the other hand, with the proceeding of the air oxidation, the polymerization degree of $-Ar-Ar-$ is increasing slightly in the part dissolving in the toluene solvent. Therefore, the blue luminescence quantum yields of b₂ and b₃ are at 10.2 and

Table 2. The extracted yield and molecular weight of extracted parts which are obtained from coal tar pitches treated under conditions with and without heating process

Samples	Extracted parts obtained by the use of toluene solvent		Extracted parts obtained by the use of pyridine solvent	
	yield, %	molecular weight	yield, %	molecular weight
Coal tar pitches without heating	6.4	452	21.4	827
Coal tar pitches heated for 30 min	6.9	542	18.2	906
Coal tar pitches heated for 60 min	8.1	614	14.3	929

Table 3. Conductivities of extracted parts obtained from coal tar pitches with and without heating process are doped by the mixture solutions () of ethanol containing iodine in different concentrations, wt %

	Samples , wt %	Coal tar pitches without heating process			Coal tar pitches heated for 30 min			Coal tar pitches heated for 60 min		
		1	5	7	1	5	7	1	5	7
Extracted parts using the toluene										

9.1% respectively, which is higher than the b_1 of 7.4%, this fact leads us to suggest the formation of $-Ar-Ar-$ structures which possibly increase the PL properties of extracted parts which dissolve in the toluene solution.

On the other side, in the case of using the extractive solution of pyridine, compared with the c_1 ($\lambda_{max} = 253$ nm), the λ_{max} of c_2 and c_3 showed 9 nm red shifts attributed to the polymerization degree of $-Ar-Ar-$ which also increased when the air oxidization was proceeding continuously, leading that π -conjugated properties extended slightly. This result is associated with the fact that the pyridine solvent can extract the parts having relative high molecular weight which are similar to the oligomers (Table 2). The luminescence quantum yields of extracted oligomers are at 7, 9.2, and 8.6%, respectively, which is consistent with the general tendency of π -conjugated polymers according to which luminescence quantum yields are extending with the increase in molecular weight. Nevertheless, it is lower than the luminescence quantum yields of extracted parts obtained by extraction with using the toluene solvent, because the extracted parts are not π -conjugated oligomers completely, since the parts of bonding structures such as $-Ar-R-COO-R-Ar-$ and $-Ar-R-O-R-Ar-$ exist mainly when the air oxidization proceeds continuously [25, 26]. Therefore, the defects of structures in extracted polymers possibly affect the increase in luminescence quantum yields.

The correlation evidence about conversions of structures which are associated with the optical properties is observed in the measurements of FTIR (Fig. 3). For example, comparing with the Fig. 3a, the peak intensities around 747–878 and 3043 cm^{-1} , which are attributed to the aromatic groups, became strong, indicating that

extracted parts obtained by toluene solvent have relative high ratio of bonding type as $-Ar-Ar-$ when the air oxidization reaction of coal tar pitches is carried out at 350°C in the initial stage (Fig. 3b). Meanwhile, the peak of 2957 cm^{-1} assigned to the existence of $-COOH$ group clearly reveals that $-COOH$ groups do not participate into the polycondensation in coal tar pitches entirely, for the extracted materials showed the low molecular weight (Fig. 3b, Table 1).

On the case using the extraction solution of pyridine, compared with the Fig. 3b, the peak of 2957 cm^{-1} of $-COOH$ group disappeared in Fig. 3d. Meanwhile, in Fig. 3d, the peak intensities of 1020 and 1121 cm^{-1} which are possibly attributed to the groups of $-COO-$ and $-C-O-$, respectively, became stronger than those in Fig. 3b, which leads us to consider that content of units such as $-COO-$ and $-C-O-$ in structures of oligomers increases. Simultaneously, in Fig. 3d the peaks of 747–880 cm^{-1} attributed to the aromatic groups became weaker than those in Fig. 3b. These results indicate that aromatic groups participated into the polycondensation and were mainly bonded by bonds such as $-Ar-R-COO-R-Ar-$ and $-Ar-R-O-R-Ar-$ in the extracted oligomers which were obtained by the extraction of pyridine solvent.

Moreover, in order to extend the applications of extracted parts, we evaluated the conductive properties of extracted oligomers with and without doping of iodine by the two-terminal method measurement (Table 3). Firstly, it was not observed the conductivities of heated coal tar pitches without doping of iodine completely. By comparison, as shown in Tables 2 and 3, with the increasing of molecular weight and doping amount of

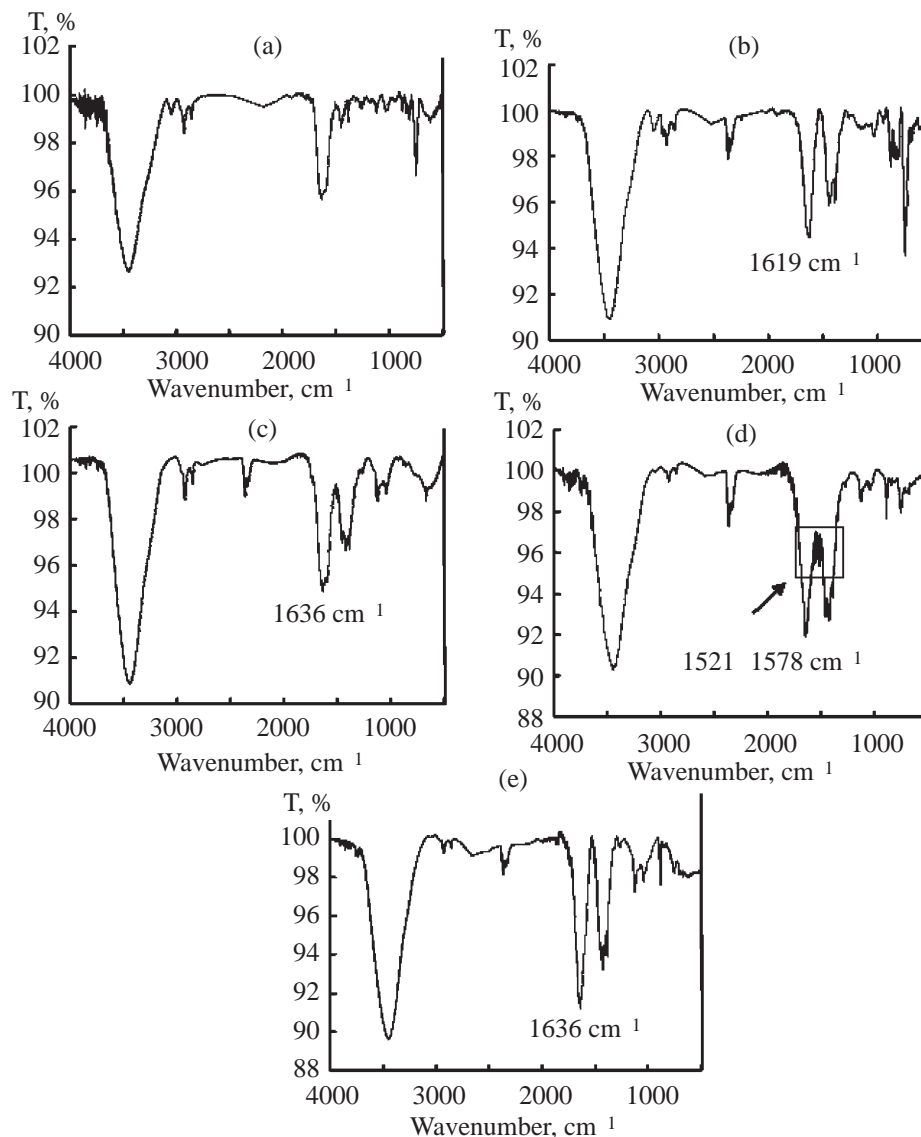


Fig. 3. (a) Result of coal tar pitches without heating process; (b) FTIR result of extracted parts of coal tar pitches heated for 60 min which are obtained by use of the toluene extraction solvent; (c) FTIR result which shows that extracted parts obtained by use of extraction solvent are doped by iodine of 7 wt %; (d) FTIR result of extracted parts of coal tar pitches heated for 60 min which are obtained by the use of the pyridine extraction solvent; (e) FTIR result of extracted parts of coal tar pitches heated for 60 min obtained using the pyridine extraction solvent doped by iodine of 7 wt %.

iodine, the conductivity of doped extracted parts shows the increasing tendency.

Specifically, the doped parts having the relatively low molecular weight show the higher conductivity than the oligomers extracted using the pyridine solvent, which can be explained by the fact that the structures of the obtained oligomers are mainly bound by the ester and ether structures that limit the extending of the π -conjugated property (Table 3). On the other hand, the conductivities of oligomers extracted using the pyridine solvent show

the tendency of increase in conductivity with increasing molecular weight, which suggests that conductivities are attributed to the increase of π -stacking among the aromatic rings in the extracted oligomers at solid state, since these oligomers have relatively high molecular weight.

To analyze the reasons of influence of iodine on the extracted materials, we carried out the analysis of FTIR measurements. Based on the comparison of FTIR results between the extractive parts with and without doping

process of iodine, we investigated the conversions of their structures. For example, on the case of using the extraction solution of toluene, as shown in Figs. 3b and 3c, compared to the peak intensities of methylene groups around 2923 cm^{-1} , the peak intensities of $747\text{--}878\text{ cm}^{-1}$ decreased remarkably when the extractive parts were doped by iodine, which indicates the iodine mainly affects the parts of aromatic groups which do not completely participate into the polycondensation at initial stage of polycondensation. At the same time, the peaks attributed to the aromatic groups around 1619 cm^{-1} in Fig. 3b are shifted to 1636 cm^{-1} (Fig. 3c) [27], which also leads us to suggest that this conversion is associated with the influence of iodine on the aromatic parts which still did not participate into the polycondensation.

In the case of using pyridine extraction solution, FTIR results of the extracted parts show that peaks around $1521\text{--}1578\text{ cm}^{-1}$ belonging to the aromatic rings (Fig. 3d) decreased remarkably after extracted parts were doped by iodine (Fig. 3e) [27]. However, the conversions around $747\text{--}878\text{ cm}^{-1}$ are inconspicuous, which might be explained by the fact that aromatic groups were bound entirely by such bonds as $\text{--Ar--R--COO--R--Ar--}$ and $\text{--Ar--R--O--R--Ar--}$ when the polycondensation proceeded continuously. The analogous supported evidence observed at comparison of peak of aromatic groups around 1636 cm^{-1} in Figs. 3d and 3e indicate that the unreacted parts in coal tar pitches were consumed by polycondensation fully.

Finally, considering the complexity of structures of coal tar pitches these analyses of FTIR can initially and roughly explain effect of iodine on the aromatic parts in bonding structures of extracted materials, which leads to the improvement of conductivities.

CONCLUSIONS

In summary, we successfully extracted the oligomers from coal tar pitches treated by the air oxidization method. According to the difference of solubility of oligomers in solvents of toluene and pyridine, the properties of extracted parts show different. Among them, the extracted parts obtained by the use of toluene solution have the relatively low molecular weight ($452\text{--}614$), general blue luminescence quantum yields of $7.4\text{--}10.2\%$ and remarkable semiconductive properties of $3.7 \times 10^{-4}\text{--}7.4 \times 10^{-4}\text{ S m}^{-1}$ after being doped by iodine. On the other hand, the extracted parts obtained by using

the pyridine solution have the relatively high molecular weight ($827\text{--}929$), show the general blue luminescence quantum yields of $7\text{--}9.2\%$ and semiconductive properties around $5 \times 10^{-7}\text{--}6.8 \times 10^{-6}\text{ S m}^{-1}$ after being doped by iodine. These results show that extracted oligomers have the possibilities of application in the electronic devices. Meanwhile, extracting the functional materials from coal tar pitches is able to use for solving the problem of overproduction of coal tar pitches in China. Finally, the extracted materials will be investigated in terms of the possibility of their use for the creation of electronic devices in the future.

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