Determination of the mono and dibromo derivatives ratio resulted from semiconductor bromination using ultraviolet-visible absorption spectroscopy and Gaussian peak fitting

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Abstract

The chemical-industrial production of organic semiconductor urgently needs a cheap and fast approach to determine the components' proportion of the reaction system. In this paper, the Gaussian peak fitting method was applied to process monobromo and dibromo substituted perylene diimide mixed solutions' ultraviolet-visible absorption curves. The functional relationship formula between the peak intensity ratio and the component ratio is then concluded. Finally, the field experiment of perylene imide brominating reaction can be used to confirm such formula is able to calculate the proportion of ingredients in the synthesis reaction solution system accurately.

Keywords: Perylene diimide; UV-Vis absorption spectrum; monitor reaction; quantitative analysis; bromination
Introduction

In the field of chemical experiments and its corresponding industrial production, it is necessary to monitor the composition ratio of substances in the reaction system during reacting, thereby verifying whether the reaction is successful or achieves the stopping standard. Meanwhile, due to cost efficient concern in industrial production, approaches of quantitative analysis of the composition ratio of reaction systems that are convenient and inexpensive were wildly studied.\(^1\)-\(^5\) Conventional quantitative analysis methods include Gas/liquid chromatography,\(^6\),\(^7\) Nuclear magnetic resonance,\(^8\) Raman spectroscopy,\(^9\) Ultraviolet-visible (UV-Vis) absorption spectroscopy,\(^10\)-\(^13\) etc. Among these methods, the cost of UV-Vis absorption spectroscopy is quite low, because the equipment itself is less pricey then others, and relatively easier to maintain or operate. This method requires the absorption peaks of the mixture's components are positioned at different wavelength, therefore the ratio of different absorption peak areas of the mixture could be directly calculated to obtain relevant component ratios.\(^14\) However, it is also difficult to analyze the composition ratio relationship with this method, while components' absorption peaks are close or coincide with each other.

Organic semiconductors have been widely studied and gradually realize industrial production. However, high production cost limits the practical application of this material. The aromatic ring's halogen substitution reaction is the crucial step of the preparation of organic semiconductor materials. It is no doubt that monomer halogenation is the prerequisite reaction for the preparation of semiconductor polymers by coupling polymerization, and halogenation is a vital way to modify polymers and small molecules. Nevertheless, the UV-Vis absorption peak positions of these reaction's raw materials and products are sometimes overlapping. In this case, to develop a fast, low-cost quantitative analysis method with UV-Vis absorption spectroscopy of its
corresponding reaction will significantly promote the industrialization of the organic semiconductor material industry.

Perylene diimide (PDI) is a crucial organic semiconductor material and has wide applications, such as, solar cells,\textsuperscript{15} field-effect transistors,\textsuperscript{16} photocatalyst,\textsuperscript{17} and electroluminescence.\textsuperscript{18} The UV-Vis absorption spectra of PDI molecules and their brominated products show three similar absorption peaks. The difference derives from the connection between their aromatic ring and halogen causes changes in the distribution of molecular energy levels, resulting in changes of light absorption peaks' intensity and position. In this paper, the mono- and di-bromide substituted PDI dissolved in organic solvents with different proportions, and their UV-Vis absorption spectra were tested. The absorption peaks data of each mixed solution was analyzed via Gaussian peak fitting. A curve equation could be obtained by fitting the curve relationship between the absorption peak intensity ratio and the composition ratio. Then, we operated the actual PDI brominating reaction and tested the solution's absorption spectra. Finally, obtained equation was applied to calculate the product ratio, and the real product ratio was calculated by column chromatography to verify the accuracy of the method. This paper provides a fast and low-cost method for determining the composition ratio of brominating reaction products in organic semiconductors' industrial production.

\textbf{Experimental}

\textit{Reagents and chemicals}

All reagents and chemicals were purchased from commercial sources (TCI, Acros, Sigma, or Alfa) and used without further purification except otherwise stated. CHCl\textsubscript{3} was distilled by standard procedures before used for organic synthesis.


**Apparatus**

UV-vis spectra of the solutions were obtained with a UV/VIS/NIR spectrometer (Lambda 750, PerkinElmer, Waltham, MA, USA) used a 1cm optical length quartz cell.

**Solution preparation**

0.0469 g (0.1 mmol) of 1BrPDI and 0.0548 g (0.1 mmol) of 2BrPDI were weighed in two conical flasks and dissolved in 100 mL dichloromethane, respectively. After the sample is fully dissolved, measure and obtain the above two solutions in different proportions and mix them in a volumetric flask, dilute to 100 mL with dichloromethane to get 1BrPDI and 2BrPDI mixed solutions in a sum concentration of 10⁻⁵ mol / L.

**Brominating reaction**

In a 200 ml three-necked flask, add PDI (0.5 g, 0.81 mmol), K₂CO₃ (0.5g, 3.63 mmol) and 30 ml of purified chloroform. Then 3 mL (58.6 mmol) or 5 mL (97.6 mmol) of liquid bromine was slowly added dropwise, heated to 60 °C, stirred and refluxed. TLC dot plate monitored the reaction. After reacted overnight, 200 mL of a saturated sodium thiosulfate solution was slowly added to the reaction solution and stirred for 30 min to remove the remaining liquid bromine. The mixture was separated by a separatory funnel to obtain the lower red organic layer, add anhydrous sodium sulfate to dry, and filter. Draw 0.5 mL filtrate and vacuum filtered in sand core funnel (Al₂O₃ as filtering layer, washed with dichloromethane), then diluted with dichloromethane to about 10⁻⁵ mol / L and tested UV-vis spectra. Pour an appropriate amount of silica gel powder in the residual filtrate and spun dry. Dichloromethane/petroleum ether (from 1:1 to 10:1) as the eluent, and purified through a chromatographic column to obtain 1BrPDI and 2BrPDI.
Results and Discussion

As shown in Fig. 1, PDI's brominating reaction is catalyzed by $\text{K}_2\text{CO}_3$, and liquid bromine was added dropwise to the chloroform suspension of PDI, then heated to reflux. In this reaction system, the raw material PDI is difficult to dissolve in chloroform, but the formed bromine products can well dissolve in chloroform, and the mono-brominating product can easily continue to react to form the dibromo product in the solution. This reaction can obtain 1 to 4 bromine-substituted products, of which 1 and 2 bromine-substituted products (1BrPDI and 2BrPDI) have a wide range of applications. People could control the reaction to produce 1BrPDI and 2BrPDI by selecting an appropriate raw material ratio and temperature, but no practical way to form one product currently. Therefore, it is necessary to quickly detect the proportion of components in the reaction mixture and select the appropriate reaction stage to quench the reaction depending on production needs.

The UV-Vis absorption spectrum curves of 1BrPDI and 2BrPDI are shown in Fig. 2. Both curves have three UV-Vis absorption peaks at wavelengths of about ~460nm (Peak 3), ~490nm (Peak 2), and ~525nm (Peak 1). The normalized curve showed that the peak intensity of 2BrPDI at ~460nm and ~490nm is higher than 1BrPDI. For the mixed solutions, the integral area of these two peaks increases as the ratio of 2BrPDI enhance. Therefore, the formula which calculates the composition ratio could be concluded through the law that these peaks change with the composition ratio.

We prepared mixed solutions under different 1BrPDI:2BrPDI mole ratios and tested their UV-Vis spectra, then used Gaussian multi-peak fitting method, which is widely applied in spectral curve analysis, to analysis the obtained spectra curves. In the Origin software, the curves were subjected to Gaussian multi-peak fitting by the following formula (1) and divided into three peaks ($A$ is the integral intensity; $\lambda$ is the
maximum absorption peak wavelength; $\omega$ is the half peak width). We noted that the curve is not matched zero in the wavelength range below 430 nm due to the background signal. Therefore, when setting the secondary peak fitting calculation, we set the background as the absorption peak to obtain a fit curve consistent with the measured absorption spectrum. Besides, we do not need to consider this background in our next calculation. The fitting curve results are shown in Fig. 3, taking the 1BrPDI: 2BrPDI=1:1 curve as an example, the other results are shown in Fig. S1. The parameters of the curve fitting result of the mixed solutions of different proportions shown in Table S1. As above-mention, the integral area of Peak 2 and 3 increases as the ratio of 2BrPDI enhance under the condition of Peak 1 as normalization. So, we plot the $(A_2+A_3)/A_1$ value as $Y$ and the mixed solution composition ratio as $X$. The resulting curve is approximately a straight line. After linear fitting, a formula for calculating the composition ratio of different brominated products in the mixed solution could be obtained.

$$y = y_0 + \frac{A_n}{\omega_n \sqrt{\frac{\pi}{4 \times \ln 2}}} \times e^{-\frac{4 \ln 2 (x-\lambda_n)^2}{\omega_n^2}} \quad (n = 1, 2, 3, 4) \quad (1)$$

To verify and improve the accuracy of our method, we repeated this experiment with elaborate operations. The UV-Vis curves were then obtained and fitted by the above method. The result parameters are shown in Table 1. Plot the $(A_2+A_3)/A_1$ value as $Y$ and the composition ratio as $X$, as shown in Fig. 4. The fitted straight-line formula is formula (2), which can be applied to calculate the composition ratio of different brominated products in the mixed solution.

$$y = 0.78267 + 0.05715x \quad (2)$$

To define this formula's practicability, we operated PDI brominating reactions with different amounts of liquid bromine (1, 3 and 5 mL). Those reactions were monitored by
thin-layer chromatography (TLC). After post-treatment, we sucked 0.5 mL of the reaction solutions and diluted by CH$_2$Cl$_2$ to achieve $\sim 10^{-5}$ mol/L level, tested the UV-Vis curves, and performed the above Gaussian peak fitting operation. The results are shown in Fig. S2 and Table 2. The $(A_2+A_3)/A_1$ values of the reaction solution with a liquid bromine amount of 1, 3 and 5 mL are 0.8019, 0.8346 and 0.8376, respectively, and the 2BrPDI mole ratios calculated by the above formula (2) are 33.6007%, 90.8641% and 96.0833%, respectively. Finally, after purification by column chromatography, the masses of the 1BrPDI and 2BrPDI products were weighed (0.1078g and 0.0592g for 1mL Br$_2$, 0.0175g and 0.2030g for 3mL Br$_2$, 0.0099g and 0.2683g for 5mL Br$_2$), and the calculated 2BrPDI mole ratios are 33.0657%, 90.7616% and 95.8556%, respectively. The results calculated by the method proposed in this paper are close to the actual purification calculation results. It is hence concluded that the method proposed in this paper has good practical prospect.

The accuracy, precision and significant difference of the proposed method was studied by literature method,$^{23, 24}$ the results are shown in Table 3. The intra- and inter-day precision values (RSD %) were both not more than 6%, while the relative error (RE %) of assay accuracies ranged from -3.13 to 2.73%. These results were within the acceptable criteria for accuracy and precision, proved that this method was reliable and reproducible for the quantitative analysis of PDI bromination. We applied the student’s t-test to study the systematic error. The calculated student’s t value ranged from 0.11 to 1.50. The two-sided critical value of students’ $t$ at the 95% confidence level for n-1 degrees of freedom was 2.78, which was greater than the calculated value suggesting there was no evidence for significant differences. It is hence we deduced that no systematic error.
Conclusions

The problem, which the organic semiconductor molecules' UV-Vis peak positions are close or coincide, hinders the UV-Vis absorption spectroscopy application in organic semiconductor industrial production. This paper studied the PDI bromination system, employed a Gaussian split peak fitting method to process the UV-Vis curve of the mixed 1BrPDI and 2BrPDI solution. According to the curve relationship between the integrated intensity ratios of different absorption peaks and the solution components' proportion, the equation of the ingredient ratio calculation for the mixed solution is obtained by the linear fitting. Real PDI bromination experiments confirmed that the result calculated by the obtained equation consistent with the actual purification calculation result. In summary, this paper provides a fast and low-cost method for determining the composition ratio of the bromination system, which has a good application prospect in organic semiconductor industrial production.

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Table 1 Gaussian multi-peak fitting result parameters of mixed solutions with different 1BrPDI:2BrPDI proportions \(^a\)

| 1BrPDI:2BrPDI | A\(_1\) | A\(_2\) | A\(_3\) | \(\lambda_1\) /nm | \(\lambda_2\) /nm | \(\lambda_3\) /nm | \(\omega_1\) /nm | \(\omega_2\) /nm | \(\omega_3\) /nm | \(R^2\) | \(\text{Chi}^2\times10^{-5}\) |
|----------------|--------|--------|--------|-------------------|-------------------|-------------------|-----------------|-----------------|-----------------|-----------|----------------|
| 10:0           | 23.30  | 14.91  | 3.28   | 522               | 487               | 456               | 22.83           | 24.62           | 19.45           | 0.999     | 5.56           |
| 9:1            | 23.50  | 15.15  | 3.39   | 522               | 487               | 456               | 23.13           | 24.82           | 19.84           | 0.999     | 5.10           |
| 8:2            | 23.79  | 15.39  | 3.54   | 523               | 488               | 456               | 23.49           | 25.04           | 20.27           | 0.999     | 4.72           |
| 7:3            | 24.31  | 15.77  | 3.73   | 523               | 488               | 457               | 23.89           | 25.35           | 20.80           | 0.999     | 4.06           |
| 6:4            | 24.83  | 16.13  | 3.90   | 523               | 488               | 457               | 24.37           | 25.67           | 21.33           | 0.999     | 3.46           |
| 5:5            | 25.18  | 16.39  | 4.03   | 523               | 488               | 457               | 24.71           | 25.87           | 21.72           | 0.999     | 3.15           |
| 4:6            | 25.48  | 16.63  | 4.13   | 523               | 488               | 457               | 24.97           | 26.07           | 22.02           | 0.999     | 2.89           |
| 3:7            | 26.08  | 17.05  | 4.33   | 523               | 488               | 457               | 25.38           | 26.39           | 22.53           | 0.999     | 2.51           |
| 2:8            | 26.39  | 17.36  | 4.45   | 523               | 488               | 457               | 25.72           | 26.73           | 23.03           | 0.999     | 2.23           |
| 1:9            | 26.61  | 17.66  | 4.58   | 524               | 489               | 457               | 25.94           | 26.99           | 23.35           | 0.999     | 2.07           |
| 0:10           | 26.87  | 17.94  | 4.68   | 524               | 489               | 458               | 26.15           | 27.24           | 23.67           | 0.999     | 1.95           |

\(a\). \(A\) is the integral intensity; \(\lambda\) is the maximum absorption peak wavelength; \(\omega\) is the half peak width; \(R^2\) is coefficient of determination; \(\text{Chi}^2\) is Residuals.

Table 2 Gaussian multi-peak fitting result parameters of PDI brominating reactions with different liquid bromine amount \(^a\)

| Br\(_2\) | A\(_1\) | A\(_2\) | A\(_3\) | \(\lambda_1\) /nm | \(\lambda_2\) /nm | \(\lambda_3\) /nm | \(\omega_1\) /nm | \(\omega_2\) /nm | \(\omega_3\) /nm | \(R^2\) | \(\text{Chi}^2\times10^{-5}\) |
|----------|--------|--------|--------|-------------------|-------------------|-------------------|-----------------|-----------------|-----------------|-----------|----------------|
| 1mL      | 24.30  | 15.76  | 3.73   | 523               | 488               | 457               | 23.90           | 25.35           | 20.80           | 0.999     | 4.08           |
| 3mL      | 26.78  | 17.72  | 4.62   | 524               | 489               | 458               | 26.15           | 27.11           | 23.57           | 0.999     | 2.00           |
| 5mL      | 26.34  | 17.51  | 4.54   | 524               | 489               | 458               | 25.78           | 26.93           | 23.26           | 0.999     | 2.31           |

\(a\). \(A\) is the integral intensity; \(\lambda\) is the maximum absorption peak wavelength; \(\omega\) is the half peak width; \(R^2\) is coefficient of determination; \(\text{Chi}^2\) is Residuals.
Table 3 Accuracy, intra- and inter-day precision, student’s t of the proposed method.

(The sample size n=5)

| 2BrPDI% | Intra-day | | Inter-day | | Student’s t |
| --- | --- | | --- | | --- | --- |
|  | Accuracy / % | RSD% | Accuracy / % | RSD% | |
| 25% | -3.13 | 4.56 | 2.73 | 5.38 | 0.57 |
| 50% | -0.25 | 3.78 | 1.72 | 2.90 | 0.11 |
| 75% | 1.04 | 2.03 | 1.56 | 3.17 | 1.50 |

a. RE (relative error)(%)=[(measured value - theoretical value) / theoretical value] × 100; b. RSD (relative standard deviation) (%) = standard deviation / average value × 100; c. Student’s t= | average value - theoretical value | × the square root of duplicates’ number / standard deviation.
Figures Captions

Fig. 1 PDI brominating reaction schematic diagram.

Fig. 2 (a) UV-Vis absorption curve (normalized) of 1BrPDI, 2BrPDI and the mixed solutions (in CH₂Cl₂). (b) An enlarged view of the dashed box area on the left Figure. The solution concentration is 1×10⁻⁵ mol/L.
Fig. 3 Gaussian multi-peak fitting result of the mixed solution's UV-Vis absorption curve (1BrPDI:2BrPDI = 1:1).

Fig. 4 Linear fitting result. The \((A_2 + A_3)/A_1\) value as \(Y\) and the percent of 2BrPDI as \(X\).
