ISSN 1027-5495. Functional Materials, 28, No.2 (2021), p. 293-300.
doi:https://doi.org/10.15407/fm28.02.293

Study on the properties of organic fluorescent materials based on triphenylamine derivatives

Xiangmin Shao

Zhengzhou University of Industrial Technology, Zhengzhou, 451150 Henan, China

Received December 15, 2020

Two triphenylamine derivatives, TTPAQ and TPA3E, were obtained. Their hydrogen nuclear magnetic resonance imaging was carried out, absorption spectra and fluorescence spectra were studied. The structures of the obtained compounds were confirmed by the data the nuclear magnetic spectroscopy. The absorption spectra showed that the maximum absorption wavelength of TTPAQ is 400 nm and that of TPA3E is 452 nm. The fluorescence spectrum showed that the TTPAQ fluorescence wavelength range is 390 ~ 650 nm, and the maximum fluorescence wavelength is 502 nm; the TPA3E fluorescence wavelength range was 449 to 701 nm, and the maximum fluorescence wavelength was 551 nm. The fluorescence quantum yields of TTPAQ and TPA3E, calculated on the basis of the reference solution, were 6.21 % and 15.28 %, respectively.

Keywords: triphenylamine, derivatives, organic fluorescent materials, fluorescent properties.

Дослідження властивостей органічних флуоресцентних матеріалів на основі похідних трифениламіну. *Xiangmin Shao*

Отримано похідні трифениламіну, TTPAQ і TPA3E. Досліджено спектри поглинання і флуоресценції. Структуру отриманих сполук визначено методом ядерної магнітної спектроскопії. Спектри поглинання показали, що максимальна довжина хвилі поглинання TTPAQ становить 400 нм, TPA3E — 452 нм. Спектр флуоресценції показав, що діапазон довжин хвиль флуоресценції TTPAQ становить від 390 до 650 нм з максимумом флуоресценції 502 нм; діапазон довжин хвиль флуоресценції TPA3E становив від 449 до 701 нм, максимум флуоресценції 551 нм. Квантові виходи флуоресценції TTPAQ і TPA3E, розраховані на основі розчину порівняння, склали 6,21 % і 15,28 % відповідно.

Получены производные трифениламина, TTPAQ и TPA3E. Исследованы спектры поглощения и флуоресценции. Структура полученных соединений подтверждена методом ядерной магнитной спектроскопии. Спектры поглощения показали, что максимальная длина волны поглощения TTPAQ составляет 400 нм, TPA3E — 452 нм. Спектр флуоресценции показал, что диапазон длин волн флуоресценции TTPAQ составляет 390 – 650 нм, максимум флуоресценции составляет 502 нм; диапазон длин волн флуоресценции TPA3E составлял 449 – 701 нм, а максимум флуоресценции составляет 551 нм. Квантовые выходы флуоресценции TTPAQ и TPA3E, рассчитанные на основе раствора сравнения, составили 6,21 % и 15,28 % соответственно.

1. Introduction

The organic fluorescent material is a kind of organic material that can emit light under external stimulation. Such a kind of organic compound has optical and electrical properties and can also be called organic semiconductors [1]. Luminescence phenomenon after stimulation by external energy also allows organic fluorescent materials to be used as a fluorescent probe in the fields

of biological imaging and tracing [2]. Modifying the molecular structure of organic fluorescent materials can change their optical properties and make them more targeted for labeling observed objects (proteins, gene fragments, etc.) [3]. When the labeled objects have got fluorescence properties, they are easier to observe and no more bulky and expensive equipment is required. In [4], a new triphenylamine derivative conjugated polymer was synthesized by the static coupling method. This kind of polymer had good solubility in a low boiling point organic solvent, and the transmittance in the near-infrared region could change significantly in a short time. The authors of [5] synthesized a series of new molecules that could realize the intramolecular charge transfer by attaching strong electron-withdrawing groups to the triphenylamine. The experimental results showed that when the electron-withdrawing group is introduced into the triphenylamine, the ability of intramolecular charge transfer increases, and the fluorescence spectrum of triphenylamine in polar solvents shifts to a deep color. Through the Sonogashira crosslinking reaction, the authors of [6] obtained three kinds of triphenylamine derivatives containing a different number of 1,8-naphthalimide fragments and studied their properties. The results showed that the glass transition temperature of the derivatives was 73–96°C, the initial temperature of thermal degradation was 421–462°C, suggesting good thermal stability, and fluorescence quantum yields of the dilute solutions in nonpolar solvents of the compounds ranged from 0.063 to 0.94 while those of the solid films were in the range of 0.011–0.25. Using triphenylamine as an electron donor and phenanthrimidazole as an electron acceptor, the authors of [7] synthesized three kinds of bipolar phenanthroimidazole derivatives, namely MePPIM-TPA, ClPPIM-TPA, and BuPPIM-TPA. The experimental results showed that the three derivatives had good bipolar carrier transport properties, and the MePPIM-TPA-based undoped fluorescent organic light-emitting diodes (OLEDs) had the maximum brightness and fluorescence quantum efficiency.

In this study, three triphenylamine derivatives were prepared. The preparation correctness and fluorescence properties of the three triphenylamine derivatives were tested. The main purpose of this study is investigate the influence of derivative substituent groups on the triphenylamine derivatives to provide an effective reference for the application of organic fluorescent materials in different fields.

Among the synthetic organic compounds, aromatic amine organic compounds have excellent solubility, and their molecular structure endows them with higher thermal stability and hole mobility. Moreover, their excellent electron-donating properties can make it easier to construct derivatives and use the increased groups to adjust their luminescent properties [8]. Triphenylamine is an aromatic amine organic compound. It is composed of three benzene rings and one nitrogen atom. One hydrogen atom in each benzene ring is displaced and bonded to the nitrogen atom at the center of the overall structure to form the rotationally symmetric structure. Triphenylamine is generally positive, but since the rotationally symmetric structure composed of three benzene rings and nitrogen atoms is relatively stable in space, it also provides excellent chemical stability [9]. In terms of fluorescence properties, the added groups are generally used to enhance the fluorescence intensity and change the fluorescence color. There are many kinds of substituent groups used for producing triphenylamine derivatives, but they are usually organic compounds with relatively complex structures. Generally, there are no monoatomic or molecular substituent groups with a simple structure.

Triphenylamine is an aromatic compound due to three benzene rings. The fluorescence efficiency of this kind of organic compound is usually high. Due to the many π keys in benzene rings, as soon as the amount of such a kind of compound reaches a certain level, there is an accumulation of π keys due to the aggregation effect, causing the fluorescence quenching phenomenon; i.e., the fluorescence efficiency increases with an increase in the amount, but the fluorescence efficiency suddenly decreases when the amount exceeds a certain value. The combination with aggregation-induced emission (AIE) compounds was used to ensure fluorescence efficiency and fluorescence quantum yield to counteract the above phenomenon. AIE compounds mainly include Siloles derivatives, tetrastyrene derivatives, triphenylamine derivatives, nitrile derivatives, and derivatives containing heteroatoms.

2. Experimental

The main instruments for the experiment are shown in Table 1, and the main reagents for preparing triphenylamine derivatives are shown in Table 2.

Table 1. Main experimental equipment

Instrument	Production company	Instrument	Production company
Nuclear magnetic resonance spectrometer	Quantum Design	Ultraviolet spectrophotometer	Mettler Toledo
Fluorescence spectrometer	Langduo Technology (Beijing) Co., Ltd.		

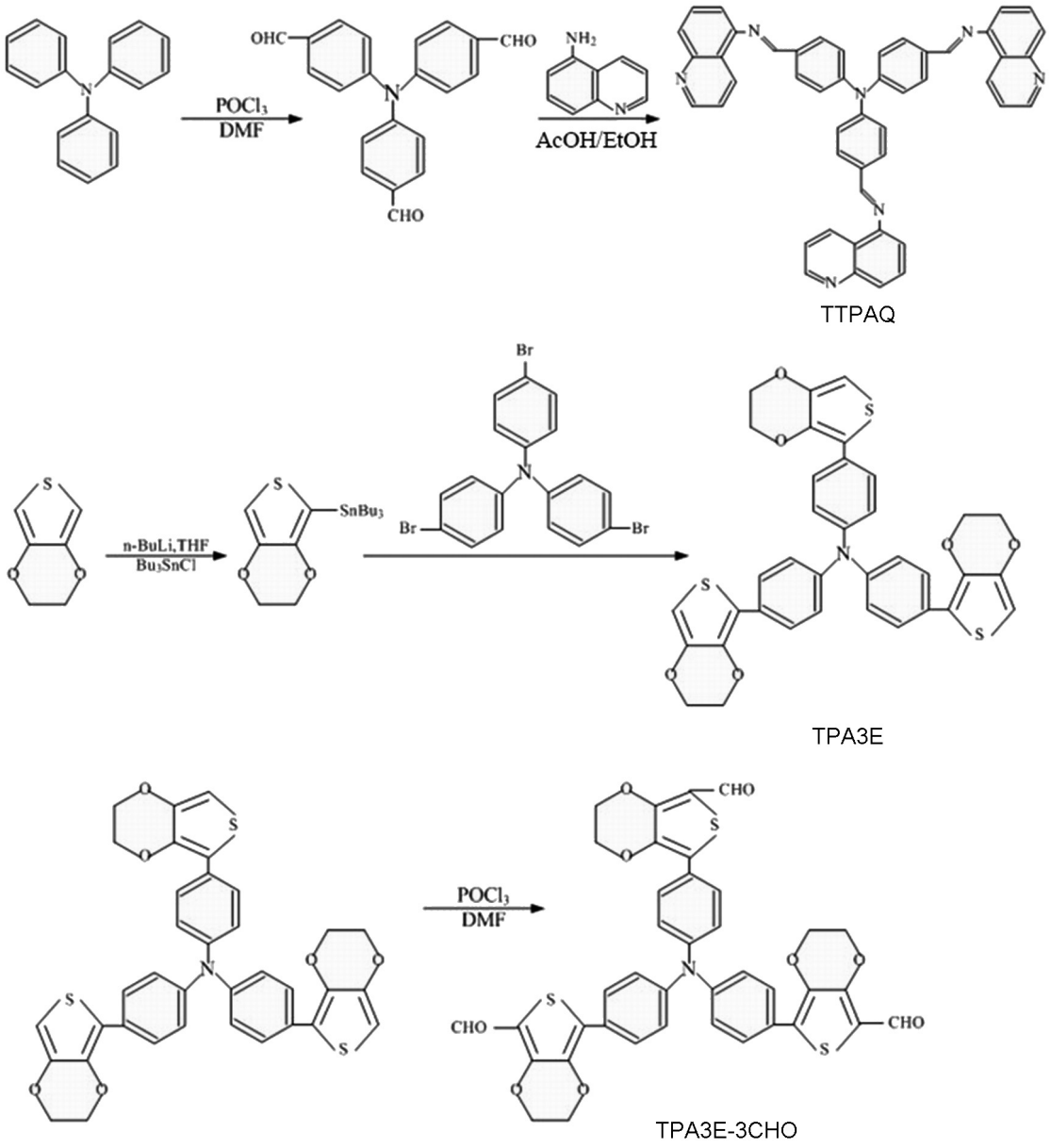

Fig. 1. Preparation route of triphenylamine derivatives TTPAQ, TPA3E, and TPA3E-3CHO.

2.1. Preparation of triphenylamine derivatives

The preparation routes of three triphenylamine derivatives, TTPAQ, TPA3E, and TPA3E-3CHO, are shown in Fig. 1. TTPAQ is a triphenylamine derivative with triphenylamine as electron-donating groups and three benzene ring electron-withdrawing groups; TPA3E is a triphenylamine derivative with one triphenylamine in the middle as electron-donating groups and three EDOT (3,4 — ethylene dioxythiophene) in three benzene ring para-positions as electron-withdrawing

Table 2. Main experimental reagents

Name of drug	Production company	Name of drug	Production company
Ethyl alcohol	Shanyi Chemical Co., Ltd.	Tetrahydrofuran	Shandong Weiming Chemical Co., Ltd.
Methyl alcohol	Shanyi Chemical Co., Ltd.	Dichloromethane	Shandong Weiming Chemical Co., Ltd. *N*, *N*′-dimethylformamide
Phosphorus oxychloride	Haorun New Energy Technology Co., Ltd.	Triphenylamine	Xidian Experimental Co., Ltd.
5-aminoquinoline	Xidian Experimental Co., Ltd.	NaOH	Cangzhou Qunyi Chemical Co., Ltd.
$MgSO_4$	Laizhou Huimei Chemical Industry Co., Ltd.	Acetic acid	Nanjing Shengqinghe Chemical Co., Ltd.
3,4-Ethylene dioxythiophene	Yacoo Technology Inc.	*n*-butyllithium	McLean
Tributyltin chloride	Haotai Chemical Co., Ltd.	Tris(4-bromophenyl)amine	Xidian Experimental Co., Ltd.
Methylbenzene	Owochem Co., Ltd.		

groups. TPA3E-3CHO is obtained by adding formyl group by DMF and $POCl_3$ based on TPA3E.

Preparation process of TTPAQ

– 15.5 mL of anhydrous DMF was cooled to the temperature below 0°C using the ice-water bath.

– Under room temperature, 19.0 mL of $POCl_3$ was added gradually to the DMF, and it was slowly stirred in the process of addition.

– 2.0 g of triphenylamine was added, stirred, and heated to 45°C.

– After 14 hours of heating, it was cooled to room temperature and added with ice water. The pH value was adjusted to neutral using NaOH.

– It was stirred for two hours under room temperature and extracted using CH_2Cl_2. The extracted organic phase was dried using anhydrous $MgSO_4$.

– Chromatographic separation was performed on the extract using a silica gel column [12] to obtain white powder: di(4-benzoyl)aniline.

– Steps (1) ~ (6) are repeated. The difference was in the category and dosage of the drugs used: 5.8 mL of DMF, 7.6 mL of $POCl_3$, and 0.98 g of di(4-benzoyl)aniline. Finally, tris(4-benzoyl)aniline was obtained.

– 1 mmol of tris(4-benzoyl)aniline and 9 mmol of 5-aminoquinoline were added to a flask. Then 6 mL of ethyl alcohol and two drops of acetic acid were added.

– After stirring at room temperature for 48 h, filtering, washing by ethyl alcohol, and recrystallization, the triphenylamine derivative, TTPAQ, was obtained. The yield was 90 %.

(2) Preparation process of TPA3E

– 3 mL of 3,4 EDOT and 80 mL of tetrahydrofuran (THF) were put into a three-necked flask. It was stirred in an environment that was filled with nitrogen under — 78°C for 30 min.

– 12.3 mL of n-butyllithium was dropwise added into the three-necked flask, followed by 120 min of reaction under the normal temperature.

– After being cooled to −78°C, 30.65 mmoL of tributyltin chloride was dropwise added. Then it was stirred and recovered to the normal temperature.

– 100 mL of deionized water was added and stirred. Then it was washed with saturated salt solution and deionized water twice. It was extracted using CH_2Cl_2 for three times. The extracted organic phase was dried using the anhydrous $MgSO_4$. Then it was filtered, and the filter liquor was processed by rotary evaporation [11] to obtain the intermediate, 3,4-EDOT-monosubstituted.

– 14.12 mmol of immediate and 4.25 mmol of tris(4-bromophenyl)amine were taken and dissolved in 50 mL of methylbenzene.

– In the nitrogen environment, 0.22 mmol of $Pd(PPh_3)_4$ was added, followed by heating reflux at 100°C for two days.

– After being cooling to room temperature, the mixture was added with 40 mL of potassium fluoride saturated solution and stirred for 12 h.

– Extraction filtration was performed. The filter liquor was washed with deionized water. Extraction was performed thrice using CH_2Cl_2. The extracted organic phase was dried using the anhydrous $MgSO_4$. Then

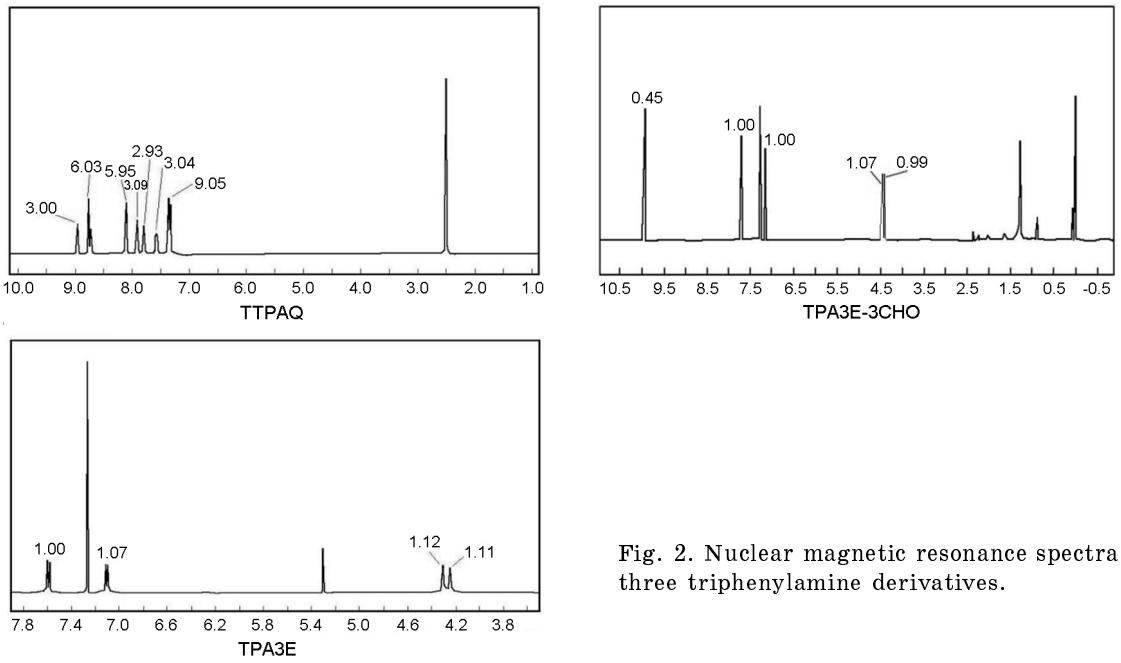

Fig. 2. Nuclear magnetic resonance spectra of three triphenylamine derivatives.

it was filtered, and the filter liquor was processed by rotary evaporation.

– The rotary evaporation product was recrystallized by methylbenzene and then separated by a silica gel column to obtain a bright yellow solid powder (chromatographic eluent: DCM/PE with a volume ratio of 1:1). The yield was 55 %.

Preparation process of TPA3E-3CHO

– 3 mL of DMF and 50 mL of 1,2-dichloroethane were added to a three-necked flask. 3 mL of $POCl_3$ was added to the flask in an environment filled with nitrogen and stirred for two hours in the ice-water bath.

– 2 mmol of TPA3E was added to the flask and refluxed for 12 hours under the condition of 80°C heating.

– It was cooled to room temperature after reflux and added with sodium hydroxide slowly to adjust the pH value to 8. 4 Extraction was performed using DCM, and the organic phase was dried using anhydrous sodium sulfate.

– The dried organic phase was filtered to remove sodium sulfate. Then, it was processed by rotary evaporation to obtain the coarse product.

– The coarse product was separated using the silica gel column chromatography to obtain the final product, TPA3E-3CHO, and the yield was 85 %.

2.3 Performance test and results for triphenylamine derivatives

(1) Obtaining the nuclear magnetic resonance spectra by a nuclear magnetic resonance spectrometer

The nuclear magnetic resonance characterization of the three triphenylamine derivatives was carried out using a nuclear magnetic resonance spectrometer produced by Quantum Design Company. The prepared TTPAQ was dissolved in deuterated dimethylsulfoxide (DMSO). TPA3E and TPA3E-3CHO were dissolved in deuterated chloroform. A nuclear magnetic resonance spectrometer was used for detection. The hydrogen nuclear magnetic resonance spectra of TTPAQ, TPA3E, and TPA3E-3CHO are shown in Fig. 2. The type of hydrogen atoms in the detected substance could be determined according to the number of peaks in Fig. 2. The height of the peaks in Fig. 2 was different, but they all were extremely high; from the peak area, the number of hydrogen atoms in the solution was detected. The extremely high peak was due to the largest amount of solvent in the solution. Therefore, there was no need to take into account the highest peak when recognizing the types of hydrogen atoms in the solution to be determined. It was seen from the nuclear magnetic resonance spectra that there were seven kinds of hydrogen atoms in TTPAQ and five kinds of hydrogen atoms in TPA3E and TPA3E-3CHO, all of which were consistent with their structural formulas.

(2) Ultraviolet-visible absorption spectrum [12] test: the wavelength range was 300 nm to 800 nm. The formula for calculation of the molar absorption coefficient of the prepared product is as follows:

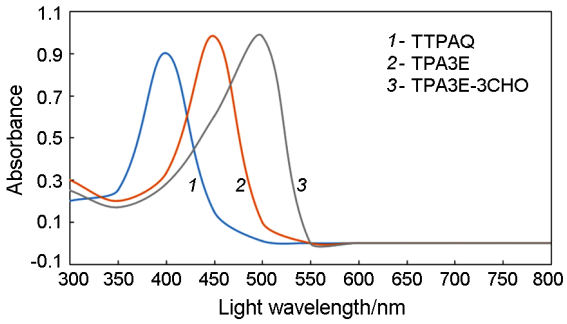

Fig.3. Ultraviolet visible absorption spectra of three triphenylamine derivatives.

$$\varepsilon = A/(cl), \quad (1)$$

where A is the absorbance of the test solution, c is the concentration of the test solution, l is the thickness of the colorimetric ware and ε is the molar absorption coefficient of the test solution. The basic steps of the test are as follows.

– TTPAQ and TPA3E solutions with a concentration of 0.1 mol/L were prepared, taking chloroform as the solvent.

– The solution to be detected was poured into a colorimetric ware. The colorimetric ware was put into an ultraviolet spectrophotometer. The absorbance under 300 nm illumination was recorded.

– Chloroform was poured into the colorimetric ware. The absorbance of the solvent under the same illumination condition was recorded for comparison. The interference of the solvent was eliminated by subtracting two absorbance values. Then, the molar absorption coefficient of the solution was calculated according to equation (1).

– The light wavelength was adjusted. Under light with a wavelength of 300, 310, 320, 330, ..., 800 nm, the molar absorption coefficient of the solution was tested according to steps 2 and 3.

The spectra of the three triphenylamine derivatives are shown in Fig. 3. The maximum absorption wavelength of TTPAQ, TPA3E, and TPA3E-3CHO was 400 nm, 452 nm, and 502 nm, respectively.

– To measure fluorescence, a chloroform solution (0.01 mM) was used as a solvent; the fluorescence quantum yield was calculated by a standard method. The formula for calculating the quantum yield of fluorescence is as follows:

$$\varphi_x = \frac{\varphi_x I_x A_s}{I_s A_x}, \quad (2)$$

where φ_x and φ_s are the fluorescence quantum efficiency of the solution to be measured and the control solution, respectively; I_x and I_s are the emission peak areas in the fluorescence spectra of the solution to be measured and the control solution, respectively; A_x and A_s are the absorbance of the solution to be measured and the control solution respectively at the same excitation wavelength. The detailed steps are as follows.

– A solution with a concentration of 0.01 mM was prepared, taking chloroform as a solvent. The solution was scanned by monochromatic light with different wavelengths to obtain excitation spectra. The maximum excitation wavelength was obtained.

– The solution was scanned by the monochromatic light with the maximum excitation wavelength to obtain the fluorescence spectrum of the solution.

– Taking 0.5 mol/L quinine sulfate solution diluted with sulfuric acid as the reference substance, the fluorescence quantum efficiency was detected using the reference method. The absorbance of the solution to be detected and contrast solution under the light with the maximum excitation wavelength was detected using a UV-visible spectrometer. The emission peak areas corresponding to the fluorescence spectra of the solution to be detected and contrast solution under the same light was obtained. Finally, calculations were performed according to equation (2).

3. Results and discussion

After obtaining ultraviolet-visible absorption spectra of the three triphenylamine derivatives in the previous experiment, the maximum absorption wavelength was taken as the excitation wavelength in the fluorescence spectrum experiment. The final fluorescence spectrum is shown in Fig. 4. Then, taking 0.5 mol/L quinine sulfate solution diluted with sulfuric acid as the reference standard, the fluorescence quantum yield of the three triphenylamine derivatives was calculated, as shown in Table 3. It was seen from Fig. 4 that the fluorescence emission peak of TPA3E was more shifted to larger wavelengths compared with TTPAQ, i.e., the fluorescence emitted by TPA3E was relatively red; the fluorescence emitted by TPA3E-3CHO was redder. The fluorescence wavelength range of TTPAQ was 390 to 650 nm (502 nm maximum), and the calculated fluorescence quantum yield was 6.21 %; the fluorescence wavelength range

Table 3. Fluorescence properties of three triphenylamine derivatives

Excitation wavelength, nm	400	452	502
Fluorescence wavelength range, nm	390 ~ 650	449 ~ 701	450 ~ 750
Maximum fluorescence wavelength, nm	502	551	601
Fluorescence quantum yield, %	6.21	15.28	20.33

of TPA3E was 449 to 701 nm (551 nm maximum), and the calculated fluorescence quantum yield was 15.28 %; the fluorescence wavelength range of TPA3E-3CHO was 450 to 750 nm (maximum at 601 nm), and the calculated fluorescence quantum yield was 20.33 %. The comparison of the above experiments indicates that the three triphenylamine derivatives have good fluorescence properties, and TPA3E-3CHO has the best fluorescence performance. The above comparison showed that TPA3E-3CHO was more suitable for the organic fluorescence field than the other two derivatives.

As an aromatic amine organic matter, triphenylamine not only has excellent solubility but also has higher thermal stability and hole mobility due to its molecular structure. Triphenylamine belongs to aromatic compounds due to three benzene rings. The fluorescence efficiency of aromatic compounds is relatively high; however, due to the presence of many bonds in the benzene ring, once the amount of aromatic compounds reaches a certain level, the superposition of bonds will be caused by effect of aggregation, which will lead to the phenomenon of quenching the fluorescence; that is, the fluorescence efficiency increases with the amount, but the fluorescence efficiency suddenly decreases when it exceeds a certain value. In order to counteract the above phenomenon, the combination with aggregation-induced emission (AIE) compounds is used to ensure fluorescence efficiency and fluorescence quantum yield. In this study, the effect of derivative groups of triphenylamine derivatives on fluorescence properties was analyzed.

Due to the variety of groups that can be added to triphenylamine, as well as the variety of position and number of bonds, triphenylamine derivatives are diverse, which increases the difficulty of research. Therefore, only three triphenylamine derivatives, TTPAQ, TPA3E, and TPA3E-3CHO, were studied in this paper. In the experiment, TPA3E-3CHO was more prone to "redshift" in UV-visible absorption spectrum than TTPAQ and TPA3E; this was due to the fact that the derivative group and

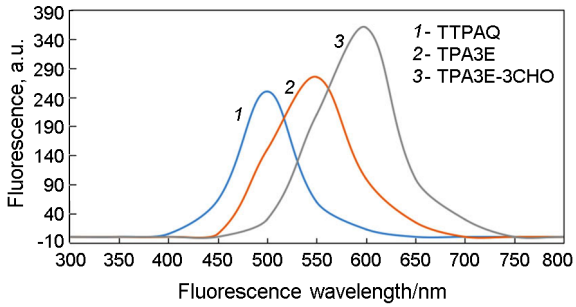

Fig. 4. Fluorescence spectra of three triphenylamine derivatives.

triphenylamine group formed a distorted configuration in the molecular structure of TTPAQ, which reduced the planarity of the molecule, while TPA3E-3CHO has a more planar molecular structure, thus the conjugated degree increased, forming a more effective π–π stacking effect and a decrease in energy required for an electronic transition in a molecule. TPA3E-3CHO has a higher degree of conjugation in terms of the fluorescence spectrum due to more planar molecular configuration, which makes the fluorescence wavelength more prone to red light and the fluorescence quantum yield higher.

4. Conclusions

In this paper, triphenylamine and its derivatives were briefly observed, as well as their fluorescence properties. Three triphenylamine derivatives, TTPAQ, TPA3E, and TPA3E-3CHO, were prepared in the experiment. Finally, the fluorescence quantum yield of the three triphenylamine derivatives was calculated using 0.5 mol/L quinine sulfate solution diluted with sulfuric acid as the reference standard. The results are as follows:

(1) the hydrogen nuclear magnetic resonance imaging spectra of the three triphenylamine derivatives accurately showed the categories of hydrogen atoms;

(2) the maximum absorption wavelength of TTPAQ, TPA3E, and TPA3E-3CHO was 400 nm, 452 nm, and 502 nm, respectively;

(3) ultraviolet-visible and fluorescence spec-

tra demonstrated that the fluorescence wavelength range of TTPAQ was 390 to 650 nm, the wavelength of the maximum fluorescence was 502 nm, and the fluorescence quantum yield was 6.21 %; the fluorescence wavelength range of TPA3E was 449 to 701 nm, the wavelength of the maximum fluorescence was 551 nm, and the fluorescence quantum yield was 15.28 %; the fluorescence wavelength range of TPA3E-3CHO was 450 to 750 nm, the wavelength of the maximum fluorescence was 601 nm, and the fluorescence quantum yield was 20.33 %.

References

1. Y.C.Chao, C.H.Chuang, H.L.Hsu et al., *Sol. Energ. Mat. Sol. C.*, **157**, 666 (2016).
2. M.P.Balanay, C.M.G.Enopia, S.H.Lee, D.H.Kim, *Spectrochim. Acta A*, **140**, 382 (2015).
3. D.Gudeika, J.V.Grazulevicius, D.Volyniuk, G.Juska et al., *J. Phys. Chem. C*, **119**, 28335 (2015).
4. S.Mi, J.Wu, J.Liu et al., *Org. Electron.*, **23**, 116 (2015).
5. R.Balasaravanan, V.Sadhasivam, A.Siva, M.Pandi, *Chem. Select*, **1**, 2792 (2016).
6. D.Gudeika, J.V.Grazulevicius, D.Volyniuk et al., *J. Phys. Chem. C*, **119**, 28335 (2015).
7. H.Peng, Z.Wei, L.Wu, X.Li, *Opt. Mater.*, **101**, 109726.1 (2020).
8. V.Thanikachalam, E.Sarojpurani, J.Jayabharathi, P.Jeeva, *New J. Chem.*, **41**, 2443 (2017).
9. A.Brzeczek, K.Karon, H.Higginbotham et al., *Dyes Pigments*, **133**, 25 (2016).
10. G.Krucaite, D.Volyniuk, J.Simokaitiene et al., *Dyes Pigments*, **162**, 196 (2019).
11. F.W.Gao, Q.C.Liang, H.L.Xu, *J. Mol. Liq.*, **311**, 113297 (2020).
12. J.Zeng, Z.Wan, H.Li et al., *Sol. Energ. Mat. Sol. C.*, **178**, 223 (2018).