

Article

Hydrogen Bond-Directed Self-Assembly of a Novel Pyrene Derivative

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Abstract: A symmetrical pyrene derivative chemical structure was prepared by a classical synthetic method such as the Sonogashira cross-coupling reaction. The molecular structure of the product was characterised in detail by nuclear magnetic resonance (NMR), mass spectrometry (MS) and other methods. Furthermore, the optical properties of the novel products were studied by UV-vis and photoluminescence spectroscopy. The electrochemical properties of the molecules were fully characterised by comparison of electrochemical experiments and DFT simulation. Scanning electron microscope (SEM) observed that the product successfully formed a regular self-assembly structure. The product verifies the role of the molecular structure of the disc-mounted molecules on the optical and self-assembly properties, and is of reference value in the field of organic optoelectronic molecules

Keywords: pyrene derivatives; self-assembly; nano/micro structures; optoelectronic applications



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1. Introduction

Organic optoelectronic materials are organic functional materials with large π -conjugated systems and photoelectric activity. Organic optoelectronic materials have the advantages of diverse structural compositions and diverse functions [1,2]. Not only that, organic optoelectronic materials can not only obtain the corresponding functions that are actually needed through molecular design, but also realise the preparation of nano-devices and molecular devices through bottom-up device self-assembly [3]. Based on this, organic optoelectronic materials are widely used in many fields, such as light-emitting diodes [4], field-effect transistors [5], organic solar cells [6], organic memories [7], biosensors [8], etc. At present, organic optoelectronic materials have attracted great attention in the fields of materials and chemistry because of their unique properties and wide applications. Molecular-level devices of π -conjugated organic molecules, molecular structure design and supramolecular self-assembly according to specific functional requirements, have become a research hotspot [9,10].

Self-assembly is a process in which the ordered supramolecular structures with new functions and characteristics are formed by using the weak interactions between molecules, including hydrophobic interaction, electrostatic interaction, hydrogen bond interaction and stacking effect [11,12]. Micro- and nano-scale fabrication of organic functional molecules via simple self-assembly is an important development direction of future scientific research. It is worth mentioning that the conjugated molecular system is the most potential molecular system for building material functional nano devices [13–15].

Pyrene is a kind of fused aromatic hydrocarbon with large planar structure which attracts the attention of many scientists for its low cost, excellent photoelectric properties

and good chemical stability [16–18]. Pyrene derivatives are widely used in nonlinear optics, photoluminescence and other fields, and have great potential for the self-assembly of disk molecules [18]. On the one hand, the pyrene nucleus facilitates the planarization of the derived molecule and thus macroscopically promotes the self-assembly of the molecule due to its electron-rich and correspondingly planar rigid structure [19–21]. On the other hand, the alkyne bond, a common structure in organic optoelectronic materials, has been shown to play an important role in improving the electron distribution and energy of the molecule and in reducing the spatial site resistance between rigid groups [22,23].

In this paper, a tetrasubstituted disc-like molecule with pyrene nucleus as the main body was prepared. The linkage of pyrene with alkynes enlarges the conjugated structure of the molecule and facilitates the fluorescence properties and π - π stacking of the molecule. Not only this, but the amide bonding contributes to hydrogen bonding and the alkane molecules in the side chain also contribute to the solubility of the molecule. These also have a positive effect on the self-assembly of the molecule. The properties of this pyrene derivative were characterised and the results were also in line with expectations. The application of pyrene derivatives in organic optoelectronic materials is expanded, and also provides some reference value for the application of organic molecules in the field of optoelectronics.

2. Materials and Method

2.1. Experimental Method

Reagents were purchased from commercial sources (Energy chemical, Aladdin) and used without further purification. ^1H -NMR spectra of the samples were recorded with a BRUKER AVANCE III HD spectrometer (NMR 500 MHz, Rheinstetten, Germany) at 20 °C. The UV-vis spectra were recorded on a HITACHI U-3010 spectrophotometer, Tokyo, Japan. The fluorescence spectra were recorded on a HITACHI F-4500 fluorescence spectrophotometer (Tokyo, Japan). FT-IR spectroscopy was recorded on a Perkin Elmer LR-64912C spectrophotometer (Waltham, MA, USA). MALDI-TOF-MS (time-of-flight mass spectrometry spectra) were determined on a Shimadzu AXIMA-CFR mass spectrometer (Kyoto, Japan). SEM observation was performed with a Jeol JSM-5400/LV (Tokyo, Japan), and the accelerating voltage was 15 kV.

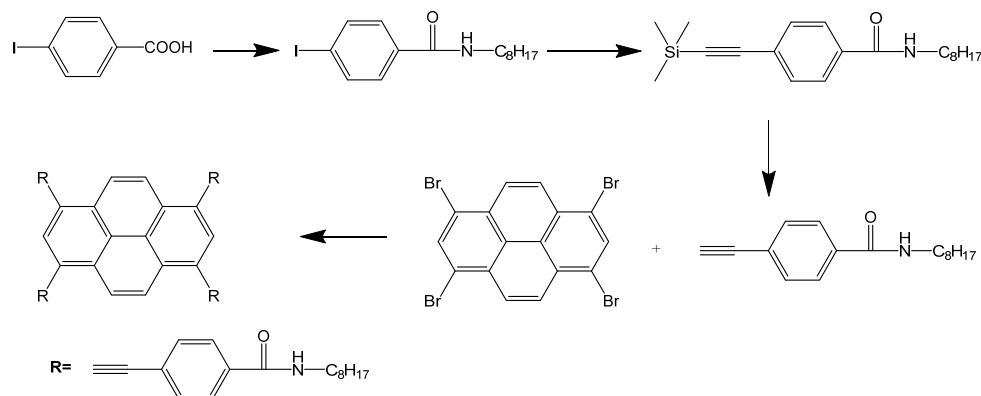
2.1.1. Synthesis of Compound 4-Iodo-N-octylbenzamide (1)

Put 1.00 g of octon-1-amine (98%, 7.7 mmol) and 1.90 g of 4-iodobenzoic acid (98%, 7.7 mmol) into a 50 mL round bottom flask, then add 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDCI, 9.0 mmol, 1.73 g) and 4-dimethylaminopyridine (DMAP, 4.0 mmol, 0.49 g) and pour 20 mL of dichloromethane (DCM, CH_2Cl_2). The reagent was reacted at room temperature for 14 h, the soluble salt was washed away with water, and then anhydrous sodium sulfate was added to dry it. The solvent was removed with evaporation, and we purified the solution using column chromatography to obtain oily compound 4-iodo-N-octylbenzamide (compound 1 in Scheme 1). Yield: (55%). ^1H NMR (500 MHz, CDCl_3): δ 7.74(m, 2H), 7.65 (m, 1H), 3.30 (q, J = 5.3 Hz, 1H), 1.59 (m, 1H), 1.33 (m, 1H), 1.30 (m, 2H), 1.28 (q, J = 2.5, 2.0 Hz, 3H), 0.89 (m, 2H). MALDI-TOF-MS (dithranol): m/z calculated for $\text{C}_{15}\text{H}_{22}\text{INO}$: 359.07 g mol^{-1} , found: 360.1 g mol^{-1} $[\text{MH}]^+$. Elemental analysis calculated (%) for $\text{C}_{15}\text{H}_{22}\text{INO}$: C, 83.28; H, 10.25; N, 6.47; found: C, 83.29; H, 10.26; N, 6.45.

2.1.2. Synthesis of Compound N-Octyl-4-((trimethylsilyl)ethynyl)benzamide (2)

Compound 1 (1.5 g, 4.24 mmol) was placed in a flask with TMSA and then catalytic reagents CuI (63.0 mg, 0.34 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (195.5 mg, 0.17 mmol) were added. The reaction was carried out at an ambient temperature of 80 °C for 8 h. After the reaction, the insoluble solid was removed using filtration, purified with column chromatography and then spun off under vacuum to obtain the solid compound N-octyl-4-((trimethylsilyl)ethynyl)benzamide (compound 2 in Scheme 1). Yield: (78%). ^1H NMR (500 MHz, CDCl_3): δ 7.91 (m, 2H), 7.64 (t, J = 5.0 Hz, 1H), 7.54 (m, 2H), 3.30 (q, J = 5.3 Hz,

2H), 1.59 (tt, 2H), 1.31 (m, 4H), 1.28 (qd, $J = 2.4, 1.1$ Hz, 6H), 0.89 (m, 3H), 0.25 (s, 7H). MALDI-TOF-MS (dithranol): m/z calculated for $C_{20}H_{31}NOSi$: 329.22 g mol⁻¹, found: 330.1 g mol⁻¹ [MH]⁺. Elemental analysis calculated (%) for $C_{15}H_{22}INO$: C, 84.15; H, 10.94; N, 4.91; found: C, 84.14; H, 10.95; N, 4.91.



Scheme 1. Molecular structure and synthetic routes of pyrene derivative TAPy.

2.1.3. Synthesis of Compound 4-ethynyl-N-octylbenzamide (3)

Compound 2 (1.18 g, 3.3 mmol) was placed in a vessel containing 10 mL of THF and 10 mL of methanol (MeOH), followed by the addition of K_2CO_3 (456.1 mg, 3.3 mmol). The whole reaction system was stirred magnetically at room temperature for 3 h and protected from light. The reaction was completed using a column (SiO_2 , DCM) and spin evaporation to obtain the solid compound 4-ethynyl-N-octylbenzamide (compound 3 in Scheme 1). Yield: (90%). ^1H NMR (500 MHz, $CDCl_3$): δ 7.87 (m, 2H), 7.62 (m, 3H), 3.30 (q, 3H), 1.59 (tt, 2H), 1.31 (m, 4H), 1.28 (m, 6H), 0.89 (m, 3H), 0.89 (m, 2H). MALDI-TOF-MS (dithranol): m/z calculated for $C_{17}H_{23}NO$: 257.18 g mol⁻¹, found: 258.3 g mol⁻¹ [MH]⁺. Elemental analysis calculated (%) for $C_{17}H_{23}NO$: C, 84.59; H, 9.61; N, 5.80; found: C, 84.59; H, 9.62; N, 5.79.

2.1.4. Synthesis of Compound TAPy

Compound 3 (0.74 g, 2.97 mmol), 1,3,6,8-tetrabromopyrene (0.38 g, 0.74 mmol), CuI (60.0 mg, 0.24 mmol) and $Pd(PPh_3)_4$ (138 mg, 0.12 mmol) were placed in a vessel containing 10 mL of tetrahydrofuran and 10 mL of triethylamine, and the reaction was stirred at 80 °C for 12 h under light-proof conditions. After the reaction, the final solid product TAPy was purified using column chromatography (SiO_2 , $V_{DCM}/V_{PE} = 1/1$) and spun off to obtain the compound. Yield: (60%). ^1H NMR (500 MHz, $CDCl_3$): δ 8.00 (s, 1H), 7.88 (m, 6H), 7.64 (t, 2H), 7.60 (m, 4H), 3.30 (q, $J = 5.3$ Hz, 4H), 1.59 (tt, 4H), 1.30 (m, 20H), 0.89 (m, 6H). MALDI-TOF-MS (dithranol): m/z calculated for $C_{84}H_{94}N_4O_4$: 1222.73 g mol⁻¹, found: 1223.9 g mol⁻¹ [MH]⁺. Elemental analysis calculated (%) for $C_{84}H_{94}N_4O_4$: C, 87.00; H, 8.17; N, 4.83; found: C, 87.02; H, 8.16; N, 4.82. FT-IR (KBr): 3270, 2925, 2853, 2210, 1636, 1545, 1312, 1049, 850.

3. Results and Discussion

3.1. Preparation Method

The synthetic route of the molecule is shown in Scheme 1, where it can be seen that the side groups were first synthesised by an amide condensation reaction and Sonogashira cross-coupling reaction [24]. After shedding the silicon atom protecting the side group [25], it was then attached to the pyrene nucleus by a Sonogashira coupling reaction, which gave the product molecule. The preparation method of the synthetic product TAPy was simple and efficient. The side alkyl molecule facilitated the solubility of the product and the amide group was also prone to hydrogen bonding, thus neutralising the spatial resistance of the

side group. In addition, the π - π stacking was facilitated by the conjugation of the pyrene structure to the triple bond, which was conducive to the self-assembly properties of TAPy.

3.2. UV-Vis and PL Spectroscopy

Figure 1 shows the UV-vis absorption spectra of TAPy solid and dissolved in dichloromethane solution. It can be seen that TAPy has characteristic absorption peaks at 345 nm and 457 nm, and, similarly, TAPy solid has a similar absorption peak to its solution, but there is another absorption peak at 510 nm. This indicates that the solid state of TAPy has a similar aggregation state and planar structure with that of the solution state, but due to the difference of the degree of molecular dispersion and the solubility in different solvents, the difference of the absorption curve appears in the solution [22,26]. On the other hand, for the fluorescence emission spectrum of TAPy (Figure 2), the absorption peak of solid TAPy has a significant redshift compared with the solution. This is also due to differences in the aggregation state and molecular morphology of the TAPy molecule [26].

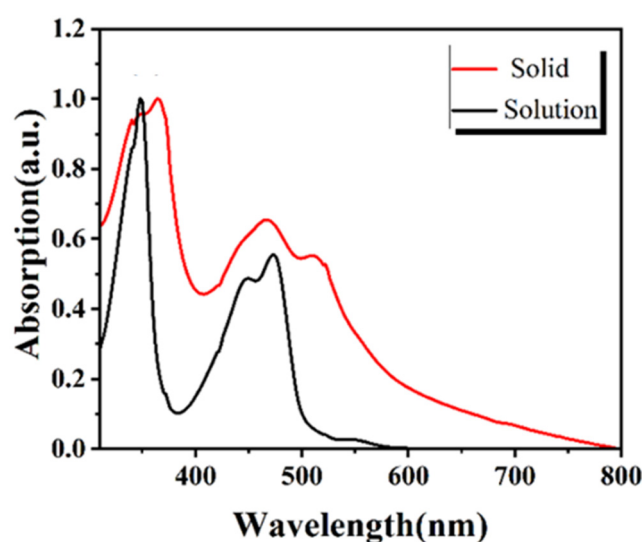


Figure 1. Normalised UV-vis absorption spectra of compound TAPy in DCM solutions and solid state.

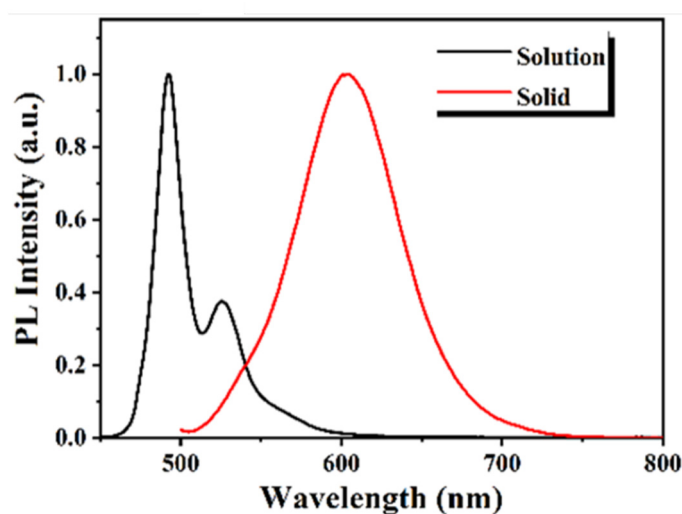


Figure 2. Normalised PL spectra of compound TAPy in DCM solutions and solid state.

For the solute discolouration effect of TAPy, Figure 3 shows the UV-vis absorption spectra of TAPy in different solvents. It can be seen that the UV absorption curves of TAPy in different solvents are almost identical. This is because the molecules have a more similar

molecular plane structure and aggregation state in these solvents (compared with solutions and solids). Figure 4 shows the fluorescence emission spectra of TAPy in different solutions, in agreement with the conclusions obtained from the UV absorption curves. It can also be seen from Table 1 that the absorption and emission peaks of TAPy in different solvents are very similar in position, which is also in line with the above conclusions.

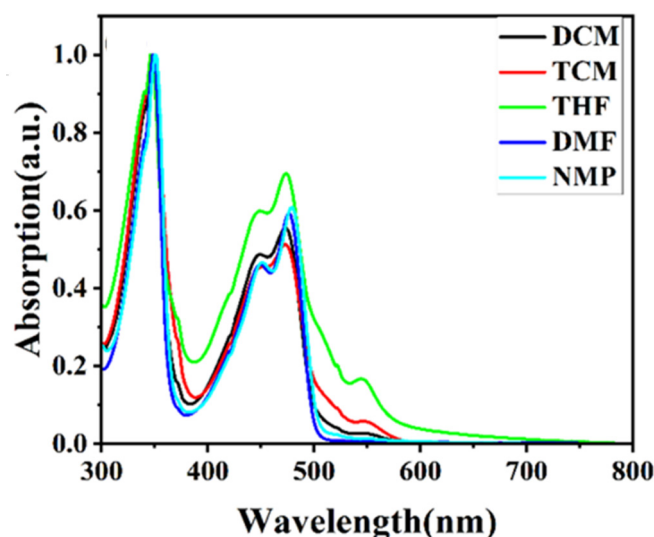


Figure 3. Normalised UV-vis absorption spectra of compound TAPy in different solvents.

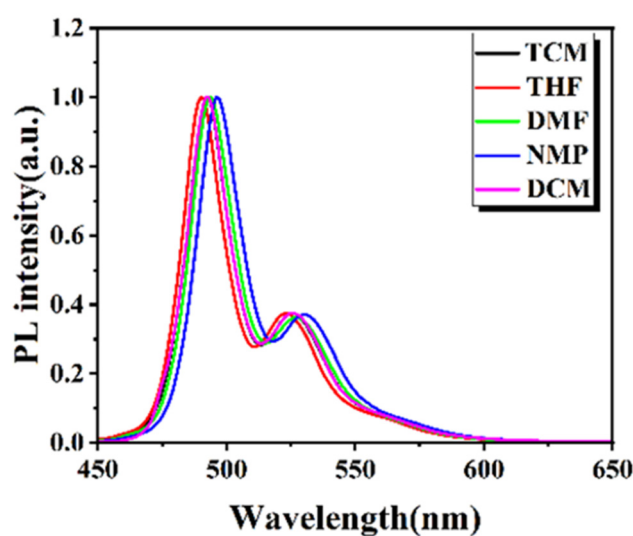


Figure 4. Normalised PL spectra of compound TAPy in different solvents.

Table 1. The positions of the highest peaks of PATy absorption and emission spectra in different solvents.

Solvent	λ_{abs} (max/nm)	λ_{em} (max/nm)	Stokes Shift (cm^{-1})
DCM (Dichloromethane)	348, 474	490, 525	868
TCM (Trichloromethane)	348, 474	492, 527	771
THF (Tetrahydrofuran)	346, 474	490, 523	688
DMF (N,N-Dimethylformamide)	348, 476	494, 527	765
NMP (N-Methylpyrrolidone)	350, 480	496, 530	672

3.3. Electrochemical Properties

The energy band structure of the product TAPy was tested with cyclic voltammetry (CA), and Figure 5 shows the cyclic-voltammetric curve of compound TAPy. According to Figure 5, the onset oxidation potential and the onset reduction potential of TAPy are approximately -1.19 eV and 0.91 eV, respectively. Further, based on the equations $E_{\text{HOMO}} = -[E_{\text{onset}}^{\text{ox}} - E_{1/2, \text{Fc}} + 4.8]$ eV and $E_{\text{LUMO}} = -[E_{\text{onset}}^{\text{red}} - E_{1/2, \text{Fc}} + 4.8]$ eV [27,28], it can be estimated that the HOMO and LUMO energy levels of TAPy are -5.51 eV and -3.41 eV, respectively.

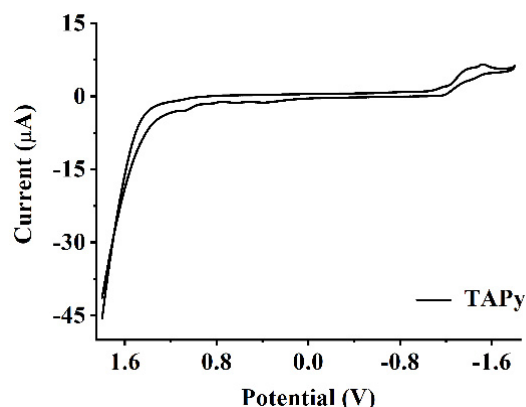


Figure 5. CV curve of TAPy measured in DCM solutions.

A schematic DFT simulation of compound TAPy is shown in Figure 6. The planar rigid structure of the olefin is linked to the pyrene structure, facilitating intramolecular charge transfer. Symmetrical electron-donating side chain groups are linked to the pyrene nucleus via the alkyne, while the pyrene nucleus of the dense ring aromatic structure becomes the acceptor. When the molecule is in the excited state, the electron distribution tends to favour the alkyne structure, whereas in the steady state the electron distribution increases in the pyrene nucleus. Not only that, because it is a symmetrical group structure, the electronic distribution of the whole molecule is symmetrical. The modification of chemical groups changes the electronic distribution of materials and thus affects their photoelectric properties [28].

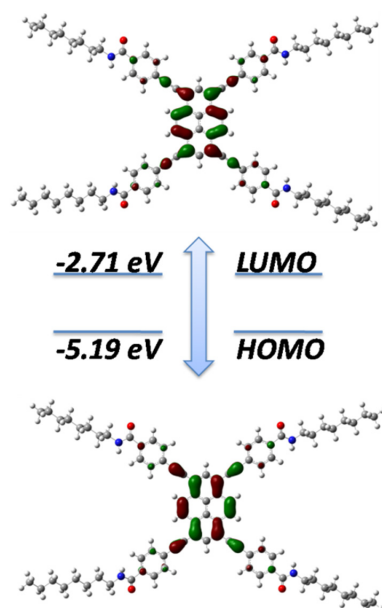


Figure 6. Density functional theory (DFT) simulation energy levels of compound TAPy.

In addition, the energy gap size of the material was also calculated from the UV absorption curve, the exact values of which we also mention in Table 2. It can be seen that the difference in the energy gap of the material calculated by the three different methods is inextricably linked to the existence of a contact potential barrier during charge injection and the exciton binding energy of the material [29].

Table 2. Electrochemical properties of the compound TAPy.

Compd	E_g^{opt} [eV] ^a	E_g^{elec} [eV]	E_g^{DFT} [eV]	$E_{\text{ox}}^{\text{onset}}$ [V]	HOMO [eV]	$E_{\text{red}}^{\text{onset}}$ [V]	LUMO [eV]
TAPy	2.38	2.10	2.48	0.91	−5.51	−1.19	−3.41

3.4. Self-Assembly Properties

When the molecule of TAPy is transferred from the benign solvent (THF) with high solubility to the poor solvent (ethanol) with low solubility, the molecule of TAPy will separate out and assemble into a regular structure by π - π^* stacking and hydrogen bonding. In the solvent with poor molecules, due to the poor interaction between the molecules and solvent, the π - π^* stacking and hydrogen bond interaction will be relatively strong, and thus the molecules will self-assemble. This is a common self-assembly method used for the self-assembly of linear nano-or micro-structures of π -conjugated organic molecules [30,31]. The self-assembly procedure consists of rapidly injecting a small volume (50 μL) of a concentrated THF supersaturated solution of TAPy (0.001 M) into a larger volume (5 mL) of ethanol and mixing immediately (as shown in Figure 7).

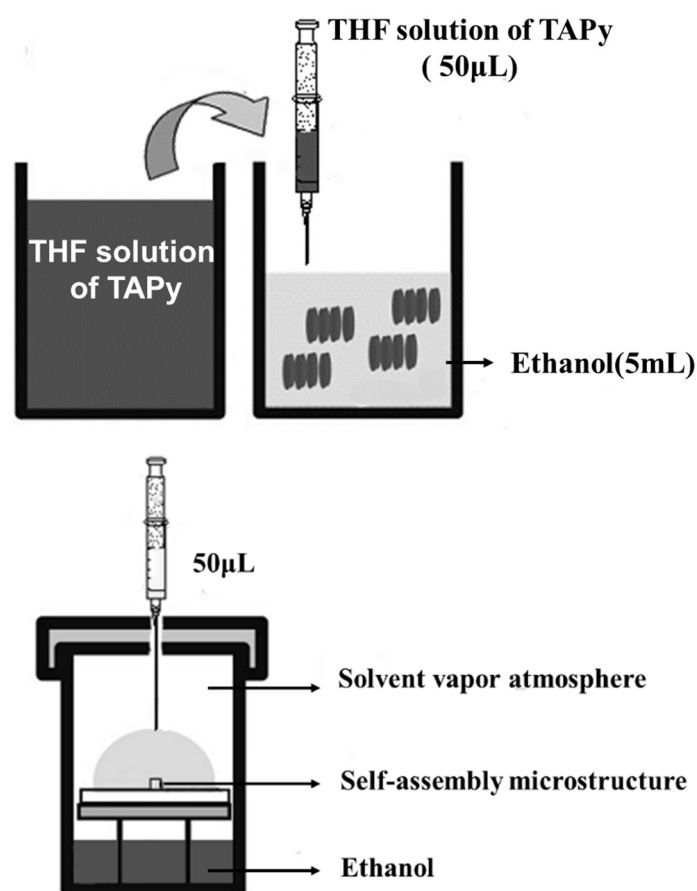


Figure 7. Preparation of TAPy self-assembled microstructures.

The compound TAPy was self-assembled using a solvent-exchange method and then characterised for its morphological features. It can be seen from the SEM image of Figure 8 that the self-assembly of TAPy forms a dendritic or reticulated-like structure. Pyrene and triple bonds form a large rigid π -conjugated planar molecular structure, which promotes π - π stacking and strong intermolecular interactions, resulting in a macroscopically regular structure, while amide bonds promote the formation of different molecular bonding hydrogen bonds and also facilitate the formation of molecular self-assembly structures. The failure to produce a more dense and regular structure may be somewhat related to the spatial site resistance created by the TAPy side groups, in addition to environmental, solvent and other reasons. This has similar results to previous studies [30–32].

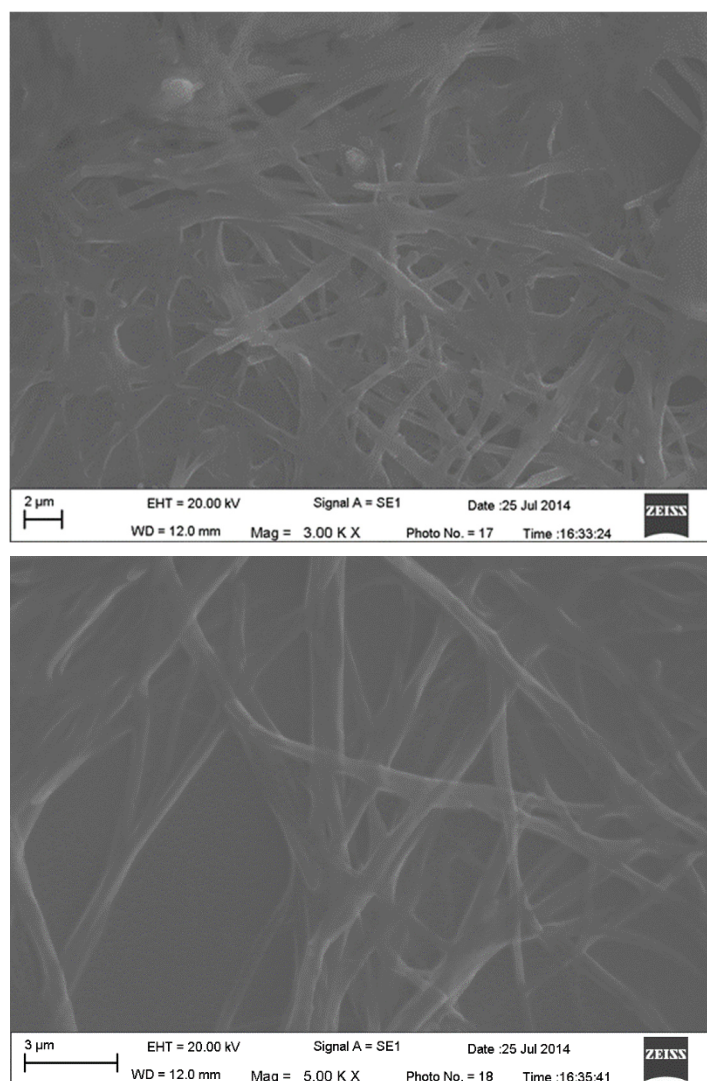


Figure 8. SEM morphologies of self-assembled TAPy by solvent-exchange method.

4. Conclusions

In summary, a tetrasubstituted group of symmetrical pyrene derivatives was designed and synthesised. The UV-vis absorption spectra and PL spectra showed that the side chain group was successfully attached to the pyrene nucleus, and the TAPy molecule had relatively excellent fluorescence performance. Electrochemical tests and DFT simulations showed that the electronic structure was altered under the influence of the substituent group, and the optical band gap was reduced by the increase in the conjugated structure. The TAPy product was self-assembled by solvent exchange followed by SEM tests, which showed that the product successfully self-assembled and formed a regular den-

drift structure, and laterally verified that the expansion of the conjugated structure and hydrogen bonding facilitated the formation of a regular self-assembled structure. The synthesis of TAPy provides a useful reference for the study of the photoelectric properties and self-assembly of conjugated discoid molecules.

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