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Synthesis, characterization and properties of a new octupolar molecule with active hydroxyl groups

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An octupolar molecule with hydroxy group was designed and synthesized. The structure and properties of the octupolar molecule were characterized by IR, EA, ^{1}HMNR, UV-vis and TG. The second order nonlinear optical property was determined by Kurtz-Perry powder method. The results showed that the octupolar molecule's SHG is 1.5 times of KDP and the maximum absorption wavelength is 412 nm. It is thermally stable with the decomposition temperature of 400 °C. Consequently it can be considered to be a better choice for the preparation of NLO materials.

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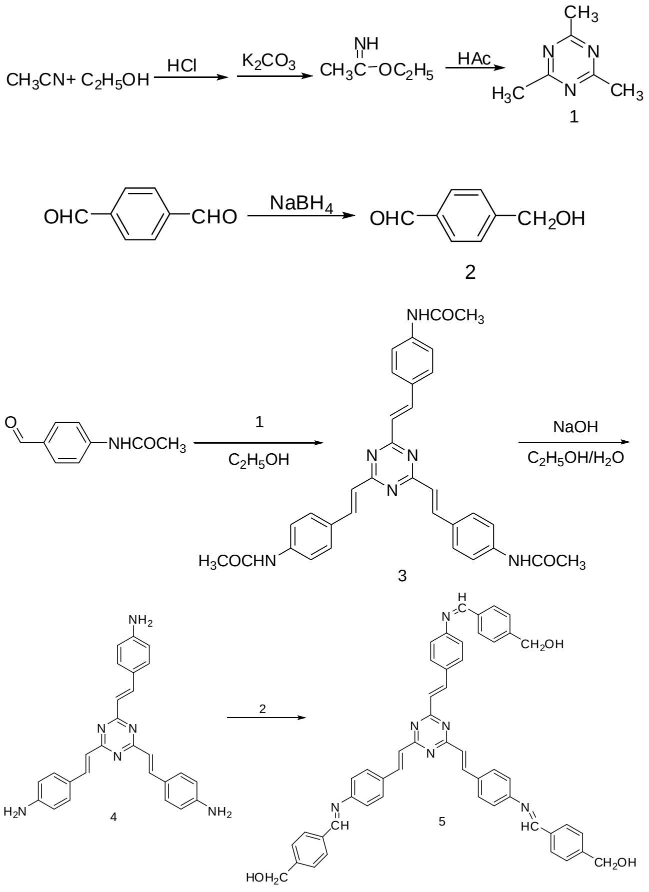
1. Introduction

Nonlinear optics is playing an important role in the fields of optical information processing, electro-optic modulation and optical switching [1–3]. Nonlinear optical (NLO) materials include inorganic and organic crystals, polymers, inorganic-organic hybrid materials [4]. Recently organic and polymeric nonlinear optical materials have drawn many attentions and have been extensively studied due to their large macroscopic optical nonlinearity, high temporal stabilities, fast response time and excellent mechanical properties [5]. Among these organic polymeric materials, push–pull molecules are important studied items for such purpose because they are composed of a donor and an acceptor moiety linked by a highly polarizable π-conjugated bridge [6], especially the D_{3h} symmetry [7]. The most common organic building block for attaining such symmetry is the 1,3,5-trisubstituted benzene residue [8]. The 2,4,6-Trimethyl-1,3,5-triazine has been intensively investigated [9] on its preparation, characterization, structural properties and chemical reactivity. In this article we designed and synthesized an octupolar molecule based on octupole system model with a s-triazine core (Scheme 1). The structure and properties of the octupolar molecule were characterized by IR, elemental analysis, ^{1}H MNR, UV-vis and TG. The second order nonlinear optical property was determined by Kurtz-Perry powder method. The results showed that it can be considered to be a better choice for the preparation of NLO materials.



Scheme 1 Synthetic route of octupolar molecule 5.

2. Experimental

2.1 Chemicals and instruments

All chemicals (analytically pure) were purchased and directly used as received unless otherwise stated. Ethanol were purified by distillation over Na and dried further over molecular sieves before being used. Column chromatography was carried out on silica gel (200–300mesh). 2,4,6-tris (styryl) -1,3,5-teriazine (1) and 4-hydroxymethylbenzaldehyde (2) were synthesized respectively following a procedure described in the literature [10-11].

The ^{1}H NMR spectra was obtained in DMSO-d6 (dimethyl sulfoxide) solution on an Inova 600 MHz spectrometer using TMS as the internal standard. TGA was undertaken on a PerinElmerDSC-2C simultaneous DTA-TG apparatus with a heating rate of 10 °C/min in the nitrogen atmosphere, and UV–vis spectra was determined on a Shimadzu240 spectrophotometer, and the margin of error is 2 nm. Elemental analysis was performed on a Carloerba-1106 micro-elemental analyzer. All measurements were performed under ambient atmosphere at room temperature.

2.2. Synthesis

2.2.1. Synthesis of 3

A mixture of 2,4,6-trimethy-1,3,5-triazine **1** 0.56 g (4.55 mmol) and N-(4-formylphenyl) acetamide 2.64 g (16.60 mmol) and KOH 0.34 g (6.00 mmol)in absolute ethanol (30 ml) was refluxed for 24 h, then cooled down to room temperature and filtered. After recrystallization from ethanol, a pale yellow solid was obtained 1.81 g (72.1%). ^{1}HNMR (DMSO-d6,600Hz) δ: 7.96 (d, J＝24 Hz, 6H, ArH), 7.62 (d, J＝12 Hz, 6H, ArH), 6.97 (d, J＝24 Hz, 6H, CH＝CH), 10.0 (s, 3H, NHCO), 2.24 (s, 9H, CH_3); IR (KBr) ν: 3308 (N-H), 2940 (CH_3), 1688 (C＝N), 1607 (C＝C), 1543, 1520, 1460 (C_6H_4) cm^{-1}. Anal.calcd for $C_{33}H_{30}N_6O_3$: C 70.97, H 5.39, N 15.54; found C, 70.85, H 5.39, N 15.66.

2.2.2. Synthesis of 4

In a round-bottom flask (100 mL), 2,4,6-tri ((4-acetamido) styryl)-1,3,5-triazine **3** 2.00 g (3.58 mmol), sodium hydroxide 8.60 g (0.215 mol) , ethanol (40 ml) and water (20 ml) were mixed. The reaction mixture was reluxed for 5 h, then cooled down to room temperature and filtered. The precipitate was dissolved in 2N HCl solution, and the solution was neutralized with sodium hydroxide. The precipitate was separated by filtering. an orange microcrystalline powder was obtained 1.28 g (82.6%). ^{1}H NMR (DMSO-d6, 600 MHz) δ: 8.01 (d, J＝18 Hz, 6H, ArH), 7.44 (d, J＝6 Hz, 6H, ArH), 6.57 (d, J＝6 Hz, 6H, CH＝CH), 5.71 (s, 6H, NH2); IR (KBr) ν: 3362 (N-H), 3010 (PhH), 1629 (C＝N), 1600 (C＝C), 1557, 1525, 1498 (C_6H_4) cm^{-1}. Anal. calcd for $C_{27}H_{24}N_6$: C 75.00, H 5.56, N 19.44; found C 74.88, H 5.53, N 19.49.

2.2.3. Synthesis of 5

2,4,6-tri((4-amino) styryl)-1,3,5-triazine **4** 1.00 g (2.31 mmol) was dissolved in 15ml DMF at room temperature, followed by the addition of 4-hydroxymethylbenzaldehyde **2** 1.15 g (6.94 mmol) at once. The mixture was stirred at 80 ℃ for 8 h, then cooled down to room temperature. The reaction mixture was poured slowly into water (50 ml). A liquid, such as coconut milk was obtained. Ammonium chloride was added slowly to the emulsion. The precipitate was separated by filtering and was crystallized from ethanol as a yellowish gray microcrystalline powder 1.4 7 g (66.2%). ^{1}HNMR (DMSO-d_6, 600 Hz) δ: 7.88 (d, J＝6 Hz, 6H, ArH), 7.76 (d, J＝6 Hz, 12H, ArH), 7.21 (d, J＝6 Hz, 6H, ArH), 7.05 (d, J＝12 Hz, 6H, CH＝CH), 8.57 (d, J＝6 Hz, 3H, N＝CH), 3.24 (t, J＝6 Hz, 6H, OCH_2), 2.50 (s, 3H, OH); IR (KBr) ν: 3365 (N-H), 3338(OH), 3020 (PhH), 1621 (C=N), 1600 (C=C), 1594, 1506, 1490 (C_6H_4) cm^{-1}; Anal. Calcd for $C_{51}H_{42}N_6O_3$: C, 77.86; H, 5.34; N, 10.69; found: C, 73.87; H, 5.35; N, 10.65.

3. Results and discussion

3.1. Synthesis

We use two methods to prepare the octupolar molecule **4**:

1) Condensation with 2,4,6-trimethy- 1,3,5-triazine and 4-aminobenzaldehyde, we could not get the expected product. The reason may be due to self –polymerization of 4-aminobenzaldehyde during the reaction process.
2) Condensation with 4-nitrobenzaldehyde and 2,4,6-trimethyl- 1,3,5-triazine which was reducted with Fe/HCl or NH_2-NH_2.H_2O. We got the expected product. We found that octupolar molecule with nitro-group almost can not dissolve in any organic solvents

In this article, we got the expected product using method 2 with the synthetic route shown in scheme 1. This method is simple, and the total yield is up to 59.6%.

3.2. UV–vis spectra

Fig. 1 shows the absorption and **UV–vis** spectra of octupolar molecule **5** in DMF. In the UV－vis absorption spectra, the absorption peak of octupolar molecule **5** is around 412 nm, displaying good transparency.

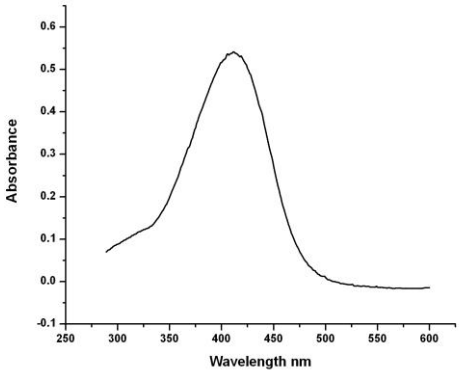


Fig. 1. UV –vis absorption spectrum of octupolar molecule 5 in DMF with the concentration of 6.0×10^{-8} *mol* L^{-1}.

3.3. Thermal properties

For optoelectronic applications, the thermal stability of organic materials is critical for device stability. The thermal property of octupolar molecule **5** is investigated by thermo gravimetric analysis (TGA) and differential thermal analysis (DTA). The analysis results are shown in Fig. 2, from which we can see that the decomposition temperature of octupolar molecule **5** is 400 °C, and could meet the temperature requirement of working and processing.

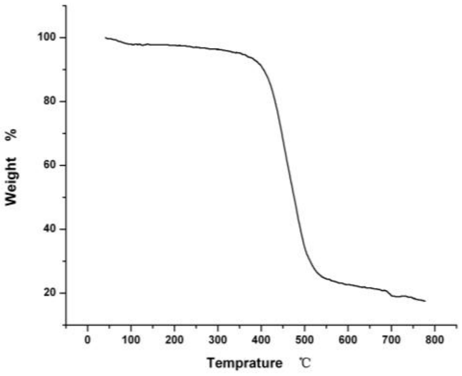


Fig. 2. TG of octupolar molecule 5.

3.3. SHG efficiency measurement

The SHG efficiency was measured for the grown crystal using the standard Kurtz and Perry powder technique [12]. The fundamental beam of a Q-switched Nd:YAG laser with a wavelength of 1064 nm. The results obtained by this method showed the SHG efficiency of octupolar molecule **5** is 1.5 times that of KDP.

4. Conclusions and future works

In this article a novel octupolar molecule was synthesized by 3-step starting from p-hydroxybenzaldehyde. The absorption peak of octupolar molecule **5** in DMF is 412 nm. It displays better thermal stability with decomposition temperature 400 °C. The SHG value of octupolar molecule **5** is 1.5 times that of KDP. The organic compound may be a potential candidate of NLO material.

Study on second-order nonlinear of octupolar molecules with threefold symmetry axis is a very important direction. In the future, we will synthesize octupolar molecule with hydroxyl which is easy to condensate with diacid chloride (Adipyl chloride, sebacoyl dichloride, dodecanedioyl dichloride, etc.) and toluene diisocyanate (TDI) to make polymer materials. It can be a very promising candidate for second-order nonlinear optical materials and this material has not yet been reported.

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