

Construction and Properties of Near Infrared AIE Materials with Cyanide Group Introduction

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Abstract

Since the concept of aggregation-induced luminescence (AIE) was first proposed by Professor Tang Benzhong in 2001, it has been widely concerned by domestic and foreign colleagues. Aie provides a new way to solve the problem of aggregation-induced fluorescence quenching. At present, AIE has developed into an international frontier field pioneered and led by Chinese scientists. Compared with traditional organic fluorescent dyes, AIE materials show some significant advantages in biological imaging applications, such as high aggregation luminescence efficiency, good photostability, strong photobleaching resistance, diverse structure, strong modifiability, adjustable absorption and emission, and good biological compatibility. However, AIE fluorescent dyes still face some challenges. For example, the luminescence of AIE materials is mostly concentrated in the UV-visible region. This part of the spectrum coincides with the absorption band of hemoglobin in mammals. In order to avoid being absorbed by tissues *in vivo* and improve tissue penetration during imaging, AIE materials that are absorbed and emitted in the near infrared region need to be designed and synthesized.

Keywords

Aggregation Induction; Trianiline; Tetraphene; Biocompatibility; Bioimaging.

1. Introduction

As emerging soft luminescent materials, macromolecules with aggregation-induced emission (AIE) properties play an important role in a variety of applications such as sensors, optoelectronics, therapeutics, printing, bioimaging, pollution elimination and stimulus response devices.[1] Fluorescent nanoparticles (NPs) represent a new set of bioimaging contrast agents, and combining AIE fluorophores into NP platforms results in AIE spots with significantly improved fluorescence efficiency and excellent photostability.[2] Fluorescent nanoparticles (FNPs) have attracted more and more attention in the biomedical field in recent years due to their unique optical properties, ease of manufacture and excellent imaging performance. Compared with traditional molecular probes, including small organic dyes and fluorescent proteins, FNPs based on aggregation-induced emission (AIE) fluorescence show significant advantages in tunable emission and brightness, good biocompatibility, excellent photo and physical stability, potential biodegradability, and easy surface functionalization.[3] Compared to today's near-infrared ECL emitters, such as semiconductor quantum dots and metal nanoclusters, TPE NCs exhibit higher ECL efficiency and excellent biocompatibility, impressively, relative to blue light photoluminescence (PL) emission (440 nm), TPE NC exhibits a large redshift ECL emission (678nm). Compared to fluorescence imaging limited by photobleaching and spontaneous fluorescence, NIR ECL emission from TPE NCs is very

beneficial for reducing background interference to visible light and achieving deeper tissue penetration, thus extending ECL emission from organic nanomaterials into the NIR region for a wider range of biological applications. [4-7]

2. Research Content

Tetraphene as a common raw material of AIE, tetraphene derivatives can be connected with different substituents to adjust its conjugate structure, cyanide group can form steric hindrance to the framework, to achieve the donor-acceptor molecular structure, because cyanide group is an electron-absorbing group, can produce electron-absorbing effect and intramolecular charge transfer effect. Some people have realized AIE effect molecules in dilute solution under non crystalline and solid crystallization by modifying cyanide group on benzene ring. The fluorescence probes with different concentrations can be complexed together to achieve accurate in vivo imaging. In this paper, the organic materials with AIE effect were prepared by attaching different amounts of cyanogroup to tetraphene derivatives.

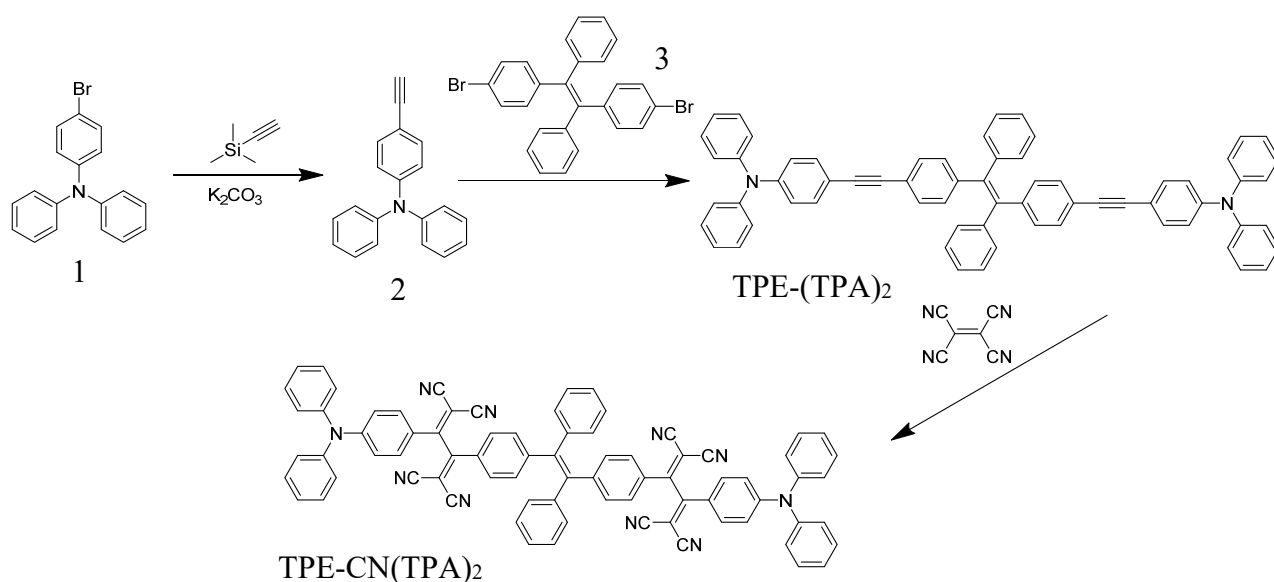


Figure 1. Synthesis route of TPE-CN(TPA)₂

The synthesis of compound 2: (6.4606 g, 20 mmol) of 1, Tetrakis(triphenylphosphine)palladium (0.578 g, 0.5 mmol), cuprous iodide CuI (0.1904 g, 1 mmol) were added to a 250 ml two-mouth round-bottomed flask with stirring agent. The stopper was wrapped with hydraulic glue to prevent air leakage. Nitrogen was pumped three times in the nitrogen pumping device. At the same time, 1:4 tetrahydrofuran and triethylamine (10 ml: 40 ml) were filled with nitrogen to drive away the air inside so as not to destroy the reaction. The temperature was set at 90°C, and the reaction was stirred for 12h. After the reaction, the mixed solution was purified by column chromatography to obtain the intermediate product. Then K₂CO₃ was added to methanol solvent and stirred at room temperature. The yellow solid powder 3 (5.743 g) was obtained by column chromatography separation and purification (DCM:PE = 1:6). Molecular weight: 269.35), yield 85%. Nuclear magnetic characterization.

The synthesis of compound TPE-(TPA)₂: The steps are similar to those for compound 2 mentioned above. Compounds 2 (0.673 g, 2.5 mmol), 3 (0.567 g, 1 mmol), Tetrakis (triphenylphosphine)palladium (0.578 g, 0.5 mmol) and CuI (0.1904 g, 1 mmol) were placed in a 100 ml two-hole flask, nitrogen was pumped three times, and then NEt₃ was added with nitrogen bubble. The reaction was set at 90°C for 12h, and the mixture was purified by column chromatography. The yield of product TPE-(TPA)₂ was 35%.

The synthesis of compound **TPE-CNTPA**: (0.15 g, 0.173 mmol) of 4 and (0.055 g, 0.4325 mmol) of tetracyanoethylene were added to a 100ml round-bottomed flask containing magnetons. The stopper of the flask was wrapped with hydraulic glue to prevent air leakage. Nitrogen was pumped three times on the nitrogen pumping device, and the replacement gas was pumped every 10-15 minutes. After replacement, 20 ml of dichloromethane was injected with a 20ml syringe. The temperature was set at 40°C, and the reaction was stirred for 8h. Product will be fully transferred to stand-up round bottom flask, spin dry on the rotary evaporator, adding suitable amount of radius is 200-300 nm of silicon powder, the bottle is washed with methylene chloride, beat until product so as to fully mix with silica powder, powder, separation and purification by column chromatography (DCM: PE = 1:2) get deep red solid powder product TPE-CNTPA (0.1846 g, Relative molecular weight: 1127.32), yield 90%.

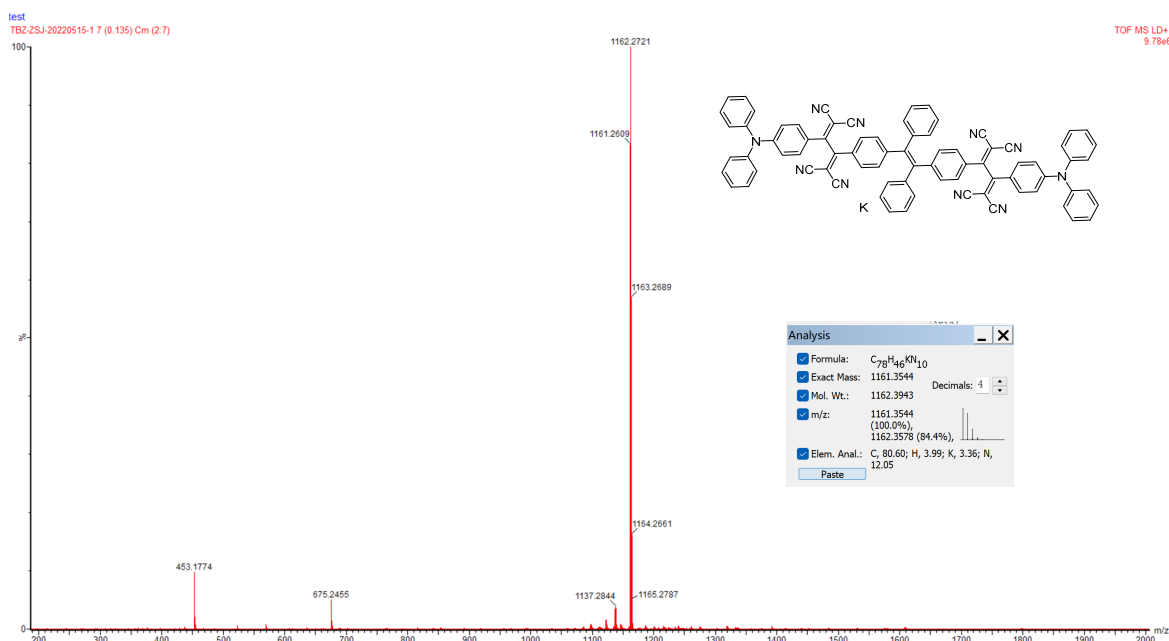
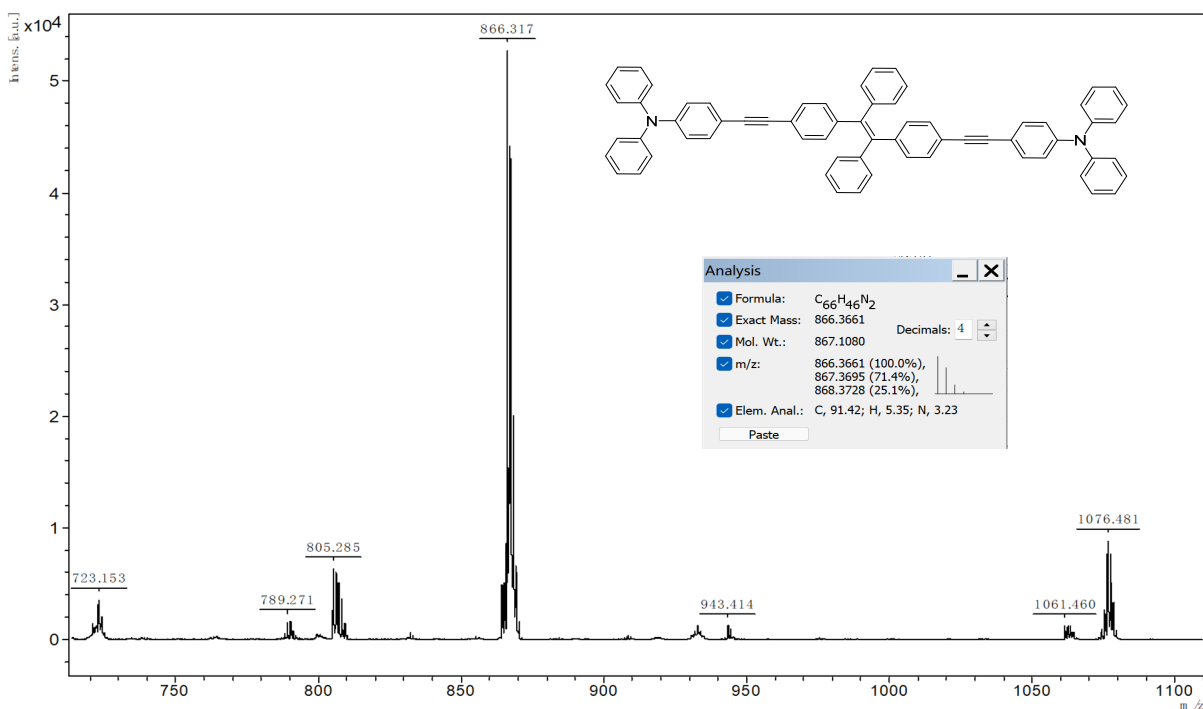


Figure 2. The mass spectrum of TPE-(TPA)₂ and TPE-CN(TPA)₂

3. Results and Discussion

3.1 Photophysical Property

As can be seen from Figure 3, after the triple bond of 4 in THF solution (10^{-5} mol/L) is replaced by cyanide group, the electronegativity is stronger after replacement because cyanide group is an electron-absorbing group, and the absorption spectrum moves directly from 370 nm to 450 nm, resulting in a red shift of 80 nm, indicating that the conjugation of the molecule has been well improved. PL spectrum also moved from the original 420 nm to 530 nm, also produced 110nm red shift, indicating that cyanogroup is an electron-absorbing group.

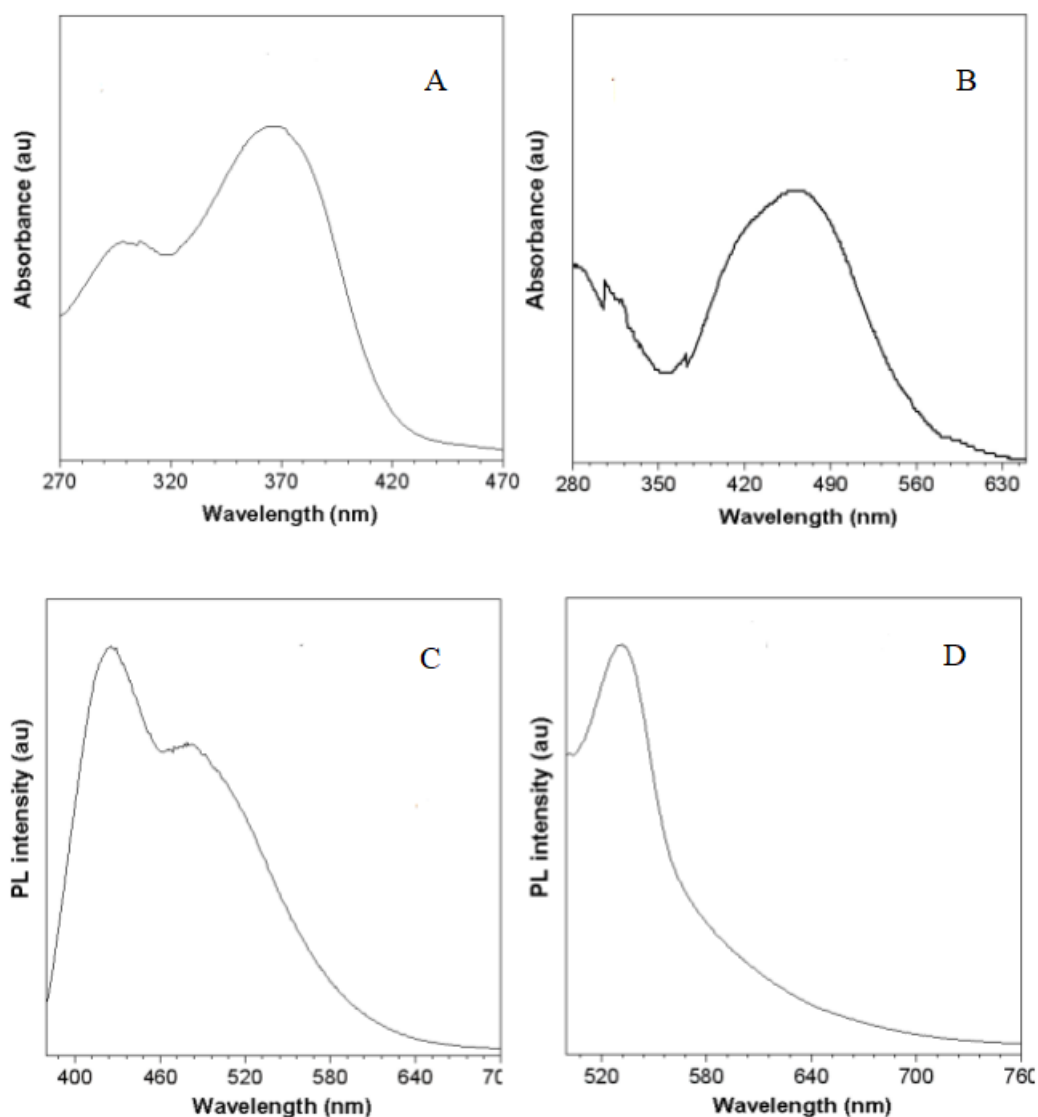


Figure 3. A and B show the absorption profiles of TPE-(TPA)₂ and TPE-CN(TPA)₂, respectively, and C and D are the PL profiles of TPE-(TPA)₂ and TPE-CN(TPA)₂

3.2 Theoretical Calculation

The spatial distributions of HOMOs and LUMOs are calculated by the Gaussian 09 program using the density functional and the M06-2X hybrid function at the 6-31G (d, p) base group level in the single molecule state. The HOMO-LUMO spatial distribution of TPE-(TPA)₂ and TPE-CNTPA are shown in Figure 4. Before the introduction of cyanogroup, HOMO of TPE-(TPA)₂ and electron cloud of LUMO are evenly distributed on the main chain. After the introduction of cyanogroup, the electron cloud of LUMO is mainly concentrated on two cyanogroups and a benzene ring of tetraphene

connected with cyanogroup. And the HOMO electron cloud is mainly on the triphenylamine on one side.

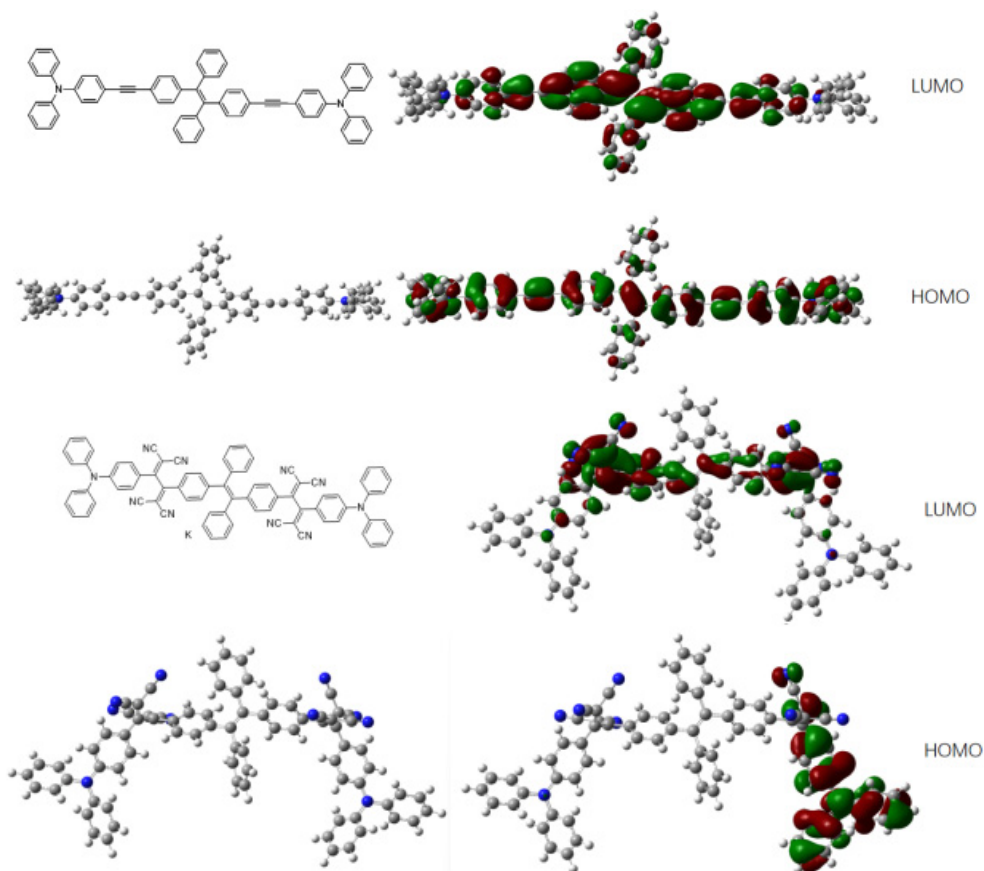


Figure 4. The HOMO-LUMO spatial distribution of TPE-(TPA)₂ and TPE-CN(TPA)₂

4. Conclusion

In this paper, TPE-CNTPA was synthesized by using TPE as core and adding trianiline. AIE material has stronger fluorescence characteristics in dilute solution. As important raw materials for AIE synthesis, trianiline and tetraphene also have stronger fluorescence characteristics. The subsequent introduction of cyanogroup has greatly changed the properties of AIE material in all aspects. It can be seen from the UV-fluorescence spectrum that the spatial conjugation degree has been greatly improved after the introduction of cyanogroup, the color becomes very dark and the polarity becomes much larger than before. Since cyanogroup is an electron-absorbing group, the addition of cyanogroup enhances the donor-acceptor interaction of the compound. The absorption and emission spectra showed obvious red shift. Electron cloud distribution also has a great tendency, from the original uniform distribution on the main chain, to concentrate on the extranet group. It is of great significance to further explore the aggregation induction properties of AIE materials.

References

- [1] Fei Zhang, Hui Xie, Bing Guo, Caizhen Zhu, Jian Xu. AIE-active macromolecules: designs, performances, and applications[J]. Polymer Chemistry, 2022, 13(01): 8-43.
- [2] Sijie Chen, Hong Wang, Yuning Hongb, BenZhong Tang. Fabrication of fluorescent nanoparticles based on AIE luminogens (AIE dots) and their applications in bioimaging[D]. Materials Horizons. 2016, 3(04): 283-293.
- [3] Lulin Yan, Yan Zhang, Bin Xu, Wenjing Tian. Fluorescent nanoparticles based on AIE fluorogens for bioimaging [J]. Nanoscale. 2016, 8(05): 2471-2487.

- [4] Jia-Li Liu, Jia-Qi Zhang, Zhi-Ling Tang Ying Zhuo Ya-Qin Chai, Ruo Yuan. Near-infrared aggregation-induced enhanced electrochemiluminescence from tetraphenylethylene nanocrystals: a new generation of ECL emitters[J]. *Chemical Science*. 2019, 10(16): 4497-4501.
- [5] Kai Li, Bin Liu. Polymer-encapsulated organic nanoparticles for fluorescence and photoacoustic imaging [J]. *Chemical Society Reviews*. 2014, 43(18): 6570-6597.
- [6] Kaojin Wang, Kamran Amin, Zesheng An. Advanced functional polymer materials[J]. *Materials Chemistry Frontiers*. 2020, 7(04): 1803-1915.
- [7] Jun Hu, Weihua Zhuang, BoXuan Ma, Xin Su et all. A two-photon fluorophore labeled multi-functional drug carrier for targeting cancer therapy, inflammation restraint and AIE active bioimaging[J]. *Journal of Materials Chemistry B* 2019, 7 (24): 3894-3908.
- [8] Hong-Wen Liu, Lanlan Chen, Chengyan Xu. Recent progresses in small-molecule enzymatic fluorescent probes for cancer imaging [J]. *Chemical Society Reviews*. 2018, 47(18): 7140-7180.