Design, Synthesis and Optical Properties of Novel D - π - a Compounds

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Abstract. New type of D - π - A compound A₁, three aniline, cyanoacetic acid and piperidine were prepared from three aniline aldehyde, propyl two nitrile and piperidine. The new D - π - A compound A₂ was prepared. The structure and fluorescence properties of the new compounds were characterized by ¹H NMR, ¹³C NMR, electron spray ionization mass spectrometry, infrared spectroscopy, UV and fluorescence spectroscopy. It can be concluded that triphenylamine Derivatives Containing Cyan and carboxyl groups have been synthesized by IR analysis. The synthesis of cyan derivatives A₁ and A₂ of triphenylamine was further illustrated by UV spectra. According to the fluorescence spectra of A₁ and A₂, the fluorescence quenching of A₁ and ibuprofen can be further determined.

Keywords: D - π - a compounds; triphenylamine derivatives; fluorescence system.

1. Introduction
D - π - a complexes are usually composed of donor - conjugated bridge - acceptor. The electron donor and the electron acceptor are connected by π bridge to form a mutual transfer system. The push-pull electrons of the electron donor and the electron acceptor cause great changes in the absorption and emission wavelengths of the structure, thus extending its application in the field of optics [1-10].

2. Instruments and Materials

2.1. Instrument
Fourier transform infrared spectrometer nexus-670 Nicolet, UV visible spectrophotometer uv-2550 Shimadzu company; Fluorescence spectrophotometer 970cert Shanghai Instrument Analysis and Manufacture General Factory; NMR spectrometer av 400 Brooke, Germany
Electron spray ionization mass spectrometer SolariX 7 Switzerland Bruker

2.2. Reagents and Materials
Piperidine (AR) Xilong Chemical Co., Ltd; Diphenylamino-4-benzaldehyde (AR) Shanghai Experimental Instrument Factory Co., Ltd; Cyanoacetic acid (AR) Tianjin Huabei Experimental Instrument Co., Ltd

2.3. Method

2.3.1. Preparation of D - π - a compound A₁. Add 0.1 g of triphenylaldehyde and 0.036 g of malononitrile into a 10 ml clean dry one mouth flask and dissolve in 5 ml of acetonitrile. Three drops of piperidine
were added dropwise and refluxed at 80 °C for 6 h. After the reaction, the solution was cooled to room temperature, poured into distilled water, filtered, washed repeatedly with distilled water for several times, and separated by column chromatography (petroleum ether: ethyl acetate = 8:1). 0.095 g yellow solid was obtained as product A1.

2.3.2. Preparation of D-π-a compound A2. Add 0.2 g of triphenylamine and 0.079 g of cyanoacetic acid into a clean, dry one mouth flask, dissolve them in 10 ml of acetonitrile, add three drops of piperidine drop by drop, reflux at 80 °C for 3 h, then cool the solution to room temperature after the reaction, pour it into distilled water, and add 10 ml of 1m 2 g purple powder was obtained by column chromatography (petroleum ether: ethyl acetate = 1:5).

2.3.3. Structural characterization of D-π-a compounds. The structures of D-π-A compounds were confirmed by nuclear magnetic resonance spectroscopy, nuclear magnetic resonance spectroscopy, electron spray ionization mass spectrometry, IR, UV and fluorescence spectra; ¹H NMR and ¹³C NMR: compounds A1 and A2 were detected by ¹H NMR and ¹³C NMR respectively with deuterated chloroform as solvent.

Electron spray ionization mass spectrometry: ionization mode is ESI-, scanning range is 100~400 m/z, compound A1 and A2 are detected by mass spectrometry in negative ion mode respectively; Infrared spectrum detection: compounds A1 and A2 were determined by potassium bromide tablet pressing method; UV detection: compounds A1 and A2 were prepared into 1.0 × 10⁻⁵ mol / L solution by using CHCl₃ as solvent, and UV / vis-265 UV VIS spectrophotometer was used for UV analysis; Fluorescence spectrum detection: Compound A1 and A2 were prepared into 1.0 × 10⁻⁶ mol / L solution with CHCl₃ as solvent, and the fluorescence emission spectrum was detected by 970 CRT fluorescence spectrophotometer.

2.4. Results and Discussion

2.4.1. Synthesis results of D-π-a compounds. The synthetic routes of compounds A1 and A2 are shown in Figure 1 and Figure 2:

![Figure 1. Synthetic route of compound A1.](image1)

![Figure 2. Synthetic route of compound A2.](image2)

First, triphenyl aldehyde was synthesized from triphenylamine, and then the cyan derivatives of triphenylamine were synthesized. In this complex, triphenylamine is used as a strong electron donor, cyan and carboxylic groups as strong electron acceptors, and C = C is an electron conjugated bridge,
thus forming two electron acceptors of D-π-a small molecular structure.

2.4.2. Structural characterization of D-π-a compounds

1H NMR analysis

CDCl₃ was used as solvent, frequency was 400 MHz, and TMS was used as internal standard. The picture shows the proton nuclear magnetic resonance spectra of compounds A₁ and A₂ and the molecular structure of the compound, and the corresponding hydrogen sites have been marked one by one, as shown in Figure 3 and Figure 4.

![Figure 3. 1H NMR spectrum of compound A₁.](image1)

![Figure 4. 1H NMR spectrum of compound A₂.](image2)

There are 15 hydrogen atoms in the 1H NMR spectrum of compound A₁, and their number is the same as that of compound A₁. The double peak of 7.02 ppm is generated by hydrogen e, and six multiple peaks of 7.19 ~ 7.32 ppm are generated by coupling hydrogen D. Four peaks of 7.35 ~ 7.39 ppm are attributed to hydrogen C, the double peaks of 7.69 ~ 7.71 ppm are attributed to hydrogen B, and the single peak of 9.81 ppm is attributed to hydrogen a. In the 1H NMR spectra of compound A₂, there are 15 hydrogen atoms, of which the double peak at 7.03 ppm is hydrogen E. Through the coupling of hydrogen D, six multiple peaks of hydrogen at 7.19-7.30 ppm are generated, and four peaks at 7.32-7.43 ppm are attributed to hydrogen C. The double peak at 7.67-7.79 ppm is designated as hydrogen B, and the single peak at 9.83 ppm is designated as hydrogen a. The hydrogen in the -COOH group of compounds A₂ is not shown in the spectrum. Because the active hydrogen on the carboxyl group exchanges rapidly with the active hydrogen in the solution, the hydrogen peak may appear in an unfixed position or not.

NMR carbon spectrum analysis

![Figure 5. 13C NMR spectrum of compound A₁.](image3)

![Figure 6. 13C NMR spectrum of compound A₂.](image4)
Compounds A1 and A2 have 8 and 9 carbons in 13C NMR spectra, respectively, corresponding to A-G and A-I carbon sites. The type of carbon in compounds A1 and A2 is consistent with the number of carbon peaks in 13C NMR spectra.

**Electron spray ionization mass spectrometry**

The ESI-MS detection reports of compounds A1 and A2 in negative ion mode are shown in Figure 7 and Figure 8. According to the ESI-MS detection report of compounds A1 and A2, it can be inferred that the peak at 320.1 M/Z is the excimer ion peak of A1. It can be inferred that the peak at 339.1 M/Z is the excimer ion peak of A2. The theoretical molecular weight of compound A1 is 321.13, the theoretical value of [M-H]. is 320.12, the measured value of [M-H]. is 320.1, the theoretical molecular weight of compound A2 is 340.12, the theoretical value of [M-H]. is 339.11, and the measured value of [M-H]. is 339.1. The results are basically consistent, which deepen the structural confirmation of compound A1 and A2. The mass of other ion peaks in A2 report is much higher than that of excimer ion peaks of compounds. It is possible that fragment ions collide with other ions or gases to produce larger ions.

![Figure 7. ESI-MS spectrum of compound A1.](image)

![Figure 8. ESI-MS spectrum of compound A2.](image)

**Infrared spectrum analysis**

The infrared spectra of compounds A1 and A2 were measured by potassium bromide tabletting method, and the results are shown in Figure 9 and Figure 10.

![Figure 9. Infrared spectrum of compound A1.](image)

![Figure 10. Infrared spectrum of compound A2.](image)

Compared with the IR spectra of the intermediate triphenylaldehyde, the keto absorption peaks of the original ligand at 1720-1700 cm⁻¹ disappeared in both spectra. In the infrared spectrum of A1, the stretching vibration peak of cyan group appeared at 2218 cm⁻¹, which further indicated the synthesis of cyan derivatives of triphenylamine. In the infrared spectrum of A2, the stretching vibration peak of carboxyl group appeared in 1720-1690 cm⁻¹, which indicated that triphenylamine Derivatives Containing Cyan and carboxyl groups were synthesized.

**Ultraviolet spectrum analysis**

The intermediate triphenylamine aldehyde and compounds A1 and A2 were dissolved in chloroform to prepare three solutions with the same concentration. The UV spectrum was scanned in the wavelength range of 250-600 nm, as shown in Figure 11. The fluorescence emission spectra of compounds A1 and A2 were scanned in the wavelength range of 400-800 nm. The scanning diagram is shown in Figure 12. When the electron withdrawing group is connected to the conjugated system in the molecule, the mobility of the electron cloud of the conjugated system increases, and the increase of the conjugated
system will also make the absorption peak red shift, which eventually leads to the maximum absorption wavelength moving to the long wavelength direction and the absorption enhancement. At the same time, when the strong absorption electron group is connected to the conjugated system in the molecule, the conjugated system in the molecule is larger, the red shift of the absorption peak is larger than that of A2, the absorption intensity is slightly enhanced, but the change degree is very small. Furthermore, the cyan derivatives A1 and A2 of triphenylamine were synthesized.

![Figure 11. UV spectrum of compounds A1 and A2 C1=1×10⁻⁵ mol/L, C2=1×10⁻⁵ mol/L, C3=1×10⁻⁵ mol/L.](image1)

![Figure 12. Fluorescence spectrum of compounds A1 and A2 CA1=1×10⁻⁶ mol/L, CA2=1×10⁻⁶ mol/L \( \lambda_{ex}(A1)=448\text{nm}, \lambda_{em}(A1)=542\text{nm}; \lambda_{ex}(A2)=442\text{nm}, \lambda_{em}(A2)=537 \text{ nm} \))](image2)

Compared with the characteristic peak of A1 compound, the fluorescence intensity of A2 compound is stronger. The blue shift of A2 is caused by the change of functional groups, but it is not obvious. The characteristic peaks of A1 compound are shown in the figure. It is not difficult to see that the fluorescence intensity of single A1 compound is about 300, but when ibuprofen is added, the fluorescence emission peak is almost unchanged, but the fluorescence intensity is significantly reduced, about half of the original.

3. Conclusions
The structures of A1 and A2 were confirmed by NMR spectroscopy (H/C), electron spray ionization mass spectrometry, IR, UV and fluorescence spectroscopy. It was concluded that cyan derivatives of three aniline and three benzylamines Containing Cyan and carboxyl groups were successfully synthesized. At the same time, by analyzing the fluorescence emission spectra of A1 and A2, we can know that ibuprofen can make the fluorescence of A1 and A2 quenched obviously, which indicates that we can further construct the fluorescence system according to the fluorescence response of A1 and A2 with ibuprofen, and test the content of ibuprofen in vitro.

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References

[1] Padalkar, V. S.; Seki, S. Chem. Soc. Rev., 2016, 45, 169–202.
[2] J. Zhao, S. Jin, Y. Weng, Y. Chen and T. Wang, Ind. Eng. Chem. Res., 2014, 53, 1308-1312.
[3] V. S. Padalkar, S. B. Chemate, S. K. Lanke and N. Sekar, J. Lumin., 2015, 168, 114–123.
[4] T, Koji et al. Synthesis and optical properties of ESIPT-active π-conjugated benzimidazole compounds: Influence of structure rigidification by ring fusion. A. J. Org. Chem., 2017.
[5] H.-M. Lv, Y. Chen, J. Lei, C. Au and S.-F. Yin, Anal. Methods, 2015, 7, 3883–3887.
[6] A. Salimi Beni, M. Zarrandi, A. R. Madram, Y. Bayat and R. Ghahary, Electrochim. Acta, 2015, 186, 504–511.
[7] J. Zhao, S. Jin, Y. Weng, Y. Chen and T. Wang, Ind. Eng. Chem. Res., 2014, 53, 1308-1312.
[8] Parada, G. A.; Markle, T. F.; Glover, S. D.; Hammarström, L.; Ott, S.; Zietz, B. Chem. Eur. J., 2015, 21, 6362–6366.
[9] J. Cheng, D. Liu, W. Li, L. Bao and K. Han, J. Phys. Chem. C, 2015, 119, 4242–4251.
[10] H. Xiao, K. Chen, D. Cui, N. Jiang, G. Yin, J. Wang and R. Wang, New J. Chem., 2014, 38, 2386–2393.