Design, Synthesis, and Aggregation-Induced Emission Characteristics of Pure Organic Blue and Yellow Light-Emitting Materials

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Abstract: In this research, quinoreoline and 2,3-dicyanopyrazine were utilized as the acceptor units, with nitrogen n-butylcarbazole acting as the donor unit to synthesize the emissive materials DNBuCz-Q and DNBuCz-DCNPy, which emit butterfly blue and yellow light, respectively. A range of mixed solvents consisting of water and acetone (CH_3COCH_3/H_2O) were employed to examine the aggregation-induced luminescence characteristics using fluorescent spectroscopy at room temperature. The results revealed that the fluorescence intensity increased as the water content rose, confirming that both materials possess aggregation-induced emission properties. Furthermore, the luminescence mechanism of the materials was investigated in accordance with the molecular design approach.

Keywords: butterfly-shaped D-A-D molecular, aggregation-induced emission, blue lighting, yellow lighting

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1. Introduction

Organic luminescent materials that exhibit aggregation-induced emission (AIE) properties have attracted considerable attention in various fields due to their unique characteristics. These materials, which possess AIE properties, are applicable in Organic light-emitting diodes[1-3], Biological imaging[4-7], Chemical sensing[8-11], and various other applications[12,13]. The Donor-acceptor (D-A) fluorescent material[14-16] has been extensively developed and utilized for its affordability, environmental friendliness, and portability. Full-color display luminescence can be achieved by adjusting the corresponding groups and configurations. However, these materials have a critical drawback of concentration quenching, which leads to reduced device performance. Researchers have engineered electron donor (D) and electron acceptor (A) components. The optical band gap of the molecule can be modulated by altering the structures of D and A.

Leveraging aggregation-induced luminescence (AIE) properties, the development of grant-acceptor materials has proven to be an effective approach to enhance material functionality[17,18].This research aims to engineer butterfly donor-receptor functional materials with AIE attributes, using quinoxaline and 2,3-dicyanopyrazine as the acceptors, and N-n-butyl carbazole as the donor, to create micro-structured blue and yellow light-emitting molecules. Specifically, DNBuCz-DCNPy is designated as the yellow light molecule, while DNBuCz-Q, featuring quinoxaline as the acceptor, functions as the blue light molecule. To explore the aggregation-induced luminescence characteristics, these molecules are considered the optimal blue and yellow light materials, respectively, and solutions of predetermined concentrations are prepared. By altering the volume ratio of water and acetone in mixed solvent systems and fine-tuning the parameters of the fluorescence spectrometer, we observe that the fluorescence intensity of both molecules intensifies with increasing aggregation, thus confirming their AIE characteristics. To visually demonstrate the variation in luminous intensity and aid students in grasping the luminescent properties, the AIE phenomenon of these materials is illustrated through changes in solution luminosity and interactive production.

2. Experimental

2.1 The synthesis of materials

2.1.1 Synthesis of the intermediate a1

To process potassium hydroxide (373.50 mmol, 20.95 g) dissolved in 50 mL of acetone, the solution was stirred at room temperature for 30 minutes. During this phase, the solution acquired a light yellow color; subsequently, the weighed carbazole (10.00 g, 60.00 mmol) was incrementally introduced into the reaction vessel. The reaction continued for 4 hours at ambient temperature, resulting in a brownish-yellow solution; then, a solution of n-bromobutane (12.30 g, 90.00 mmol) was gradually added to the mixture, and the reaction was maintained overnight. The outcome was a dark brown suspension. Upon completion of the reaction, the solution was transferred into a diluted aqueous hydrochloric acid solution, and the pH was neutralized. The solution underwent three extractions with dichloromethane (TLC thin layer chromatography detection), and the solvent was eliminated under reduced pressure. The residue was then separated and purified using pure petroleum ether, and the final recrystallization with absolute ethanol produced 8.53 g of white needle-shaped solid with an 80% yield (the synthesis process is illustrated in Figure 1). FTMS-ESI-MS (m/z) (Information S1): calculated for $C_{16}H_{17}N$ 224.139; observed: 224.143 [M] +.

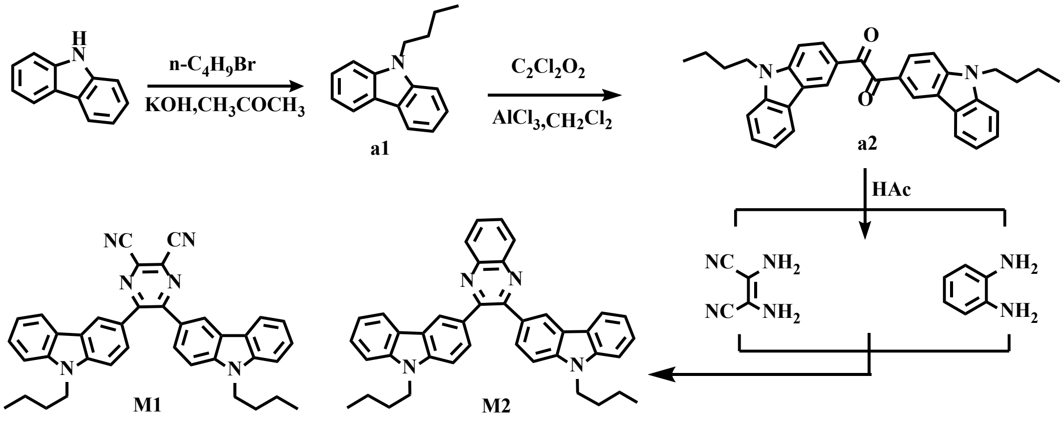

Figure 1. Material synthesis rout

2.1.2 Synthesis of the intermediate a2

Intermediate a1 (1.00g, 4.40 mmol) was dissolved in 10 mL of dry dichloromethane under an ice-salt bath with continuous stirring. Anhydrous $AlCl_3$ (0.58 g, 4.40 mmol) was then added to the reaction system in batches, resulting in an orange solution. Concurrently, intermediate a1 (1.00g, 4.40 mmol) was dissolved in another 10 mL of dry dichloromethane under an ice-cold salt bath with continuous stirring. Acetyl chloride (0.42 ml, 5.00 mmol) was then added dropwise to the system. After the addition, the solution containing oxalyl chloride was added in parallel to the solution to be prepared. At this point, the solution changed from yellow to dark blue. The reaction was allowed to proceed for 4 hours, with TLC thin layer plate tracking and monitoring. No starting material was detected, indicating the reaction had gone to completion. The reaction was then quenched and slowly poured into ice water containing dilute hydrochloric acid. The mixture was extracted with dichloromethane three times (confirmed by TLC thin plate test), followed by pressure concentration. The product was purified using column chromatography, eluting with a mixture of petroleum ether:ethyl acetate = 4:1. Recrystallization yielded 1.01 g of light yellow solid in 40% yield. (The synthesis process is illustrated in Figure 1). FTMS-ESI-MS (m/z) (Information S2): cal. for $C_{34}H_{32}N_2O_2$ 501.250; found: 501.253 [M]+.

2.1.3 The Synthesis of DNBuCz-Q (M2)

Weigh out 2.12 mmol (0.23 g) of phthalylenediamine and 1.80 mmol (0.90 g) of intermediate A 2 into a 50 mL round-bottom flask. Introduce 20 mL of glacial acetic acid and proceed with the reaction in a 100°C oil bath for 12 hours, conducting continuous monitoring. Confirm that all raw materials have been consumed before ending the reaction. Following cooling, decant the reaction mixture into saturated brine solution, carry out vacuum filtration, and keep the light green solid product. Purify by recrystallization using a 1:1 ratio of petroleum ether to dichloromethane, resulting in 0.68 g of light green powdered solid as depicted in Figure 1, achieving an 81% yield. The FTMS-ESI-MS (m/z) spectrum is depicted in Information S3: cal.for $C_{40}H_{36}N_4$ 573.297; found: 573.301[M]+. 1H NMR (500 MHz, $CDCl_3$, δ:) (Information S4) 8.49 (d, J = 1.5 Hz, 2H), 8.26 (dd, J = 6.3, 3.4 Hz, 2H), 8.00 (d, J = 7.7 Hz, 2H), 7.77 (dt, J = 6.8, 3.4 Hz, 2H), 7.57 (dd, J = 8.5, 1.7 Hz, 2H), 7.45 (td, J = 7.6, 7.1, 1.0 Hz, 2H), 7.40 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 8.6 Hz, 2H), 7.21-7.17 (m, 2H), 4.26 (t, J = 7.1 Hz, 4H), 1.81 (p, J = 7.3 Hz, 4H), 1.33 (dq, J = 14.8, 7.4 Hz, 4H), 0.88 (t, J = 7.4 Hz, 6H)

2.1.4 The Synthesis of DNBuCz-DCNPy (M1)

The synthesis procedure was identical to that described in the aforementioned material DNBuCz-Q. Recrystallization yielded 0.83 grams of a yellow powdered solid (synthesis route depicted in Figure 1), achieving a 79% yield. FTMS-ESI-MS(m/z) (Information S5): cal.for $C_{38}H_{32}N_6$ 573.272; found: 573.276[M]+. 1H NMR (500 MHz, $CDCl_3$, δ:) (Information S6)8.51 (d, J = 1.6 Hz, 2H), 7.97 (d, J = 7.7 Hz, 2H), 7.64 (dd, J = 8.7, 1.8 Hz, 2H), 7.52-7.47 (m, 2H), 7.42 (d, J = 8.2 Hz, 2H), 7.26-7.21 (m, 4H), 4.27 (t, J = 7.2 Hz,4H), 1.88-1.78 (m, 4H), 1.36 (dq, J = 14.8, 7.4 Hz, 4H), 0.91 (t, J = 7.4 Hz, 6H)

2.2 The AIE Characteristics of DNBuCz-Q and DNBuCz-DCNPy

The photophysical characteristics of the yellow-light-emitting molecule DNBuCz-DCNPy were investigated across a spectrum of water content levels, specifically at 20%, 40%, 60%, 80%, 90%, and 99%. The results indicated that with increasing water content, the aggregation of DNBuCz-DCNPy molecules became more pronounced (Figure 2b and Fig.3 right), and the fluorescence intensity exhibited an upward trend. This suggests that DNBuCz-DCNPy possesses AIE characteristics. The luminescence emission spectra labeled a and b revealed that at a water content of 99%, the peak fluorescence emission wavelength of the DNBuCz-Q (Figure 2a and Figure 3 left), molecule is approximately 475 nm, corresponding to the blue light spectrum; in contrast, the DNBuCz-DCNPy molecule's peak fluorescence emission wavelength is around 545 nm, which falls within the yellow light spectrum.

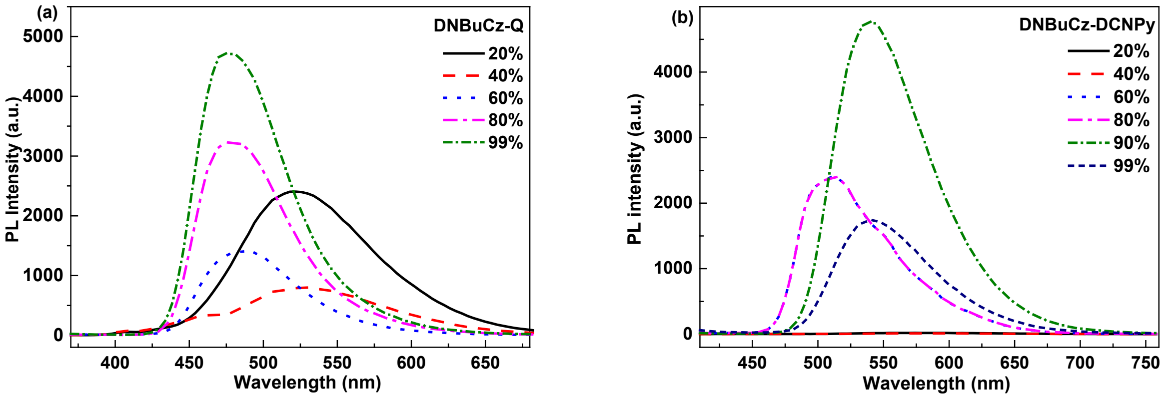

Figure 2. Fluorescence emission spectra of the luminescent molecules DNBuCz-Q (a) and DNBuCz-DCNPy (b) in different water content

Figure 3. Light-emitting molecules DNBuCz-Q (left) and DNBuCz-DCNPy (right) in different water content

The disparity in emission wavelengths among the target molecules arises from their unique acceptors: DNBuCz-DCNPy features a dicyanopyrazine acceptor, whereas DNBuCz-Q possesses a quinoxaline acceptor. The former acceptor's greater potency results in a reduced energy level gap, corresponding to the yellow light spectrum. Conversely, the latter acceptor exhibits a larger energy level difference, which gives rise to blue light emission. The AIE properties of the molecules DNBuCz-DCNPy and DNBuCz-Q stem from the fact that intramolecular rotation and vibration can occur under conditions of low water content, leading to the dissipation of most energy via nonradiative transitions, and consequently, weak luminescence. However, as aggregation becomes more pronounced, the molecules' free movement is restricted, suppressing intramolecular rotation and vibration, thereby enhancing the radiative transition path and boosting fluorescence intensity.

3. Conclusion

In this research, we harnessed dicyanopyrazine and quinololine as electron acceptors, and nitrogen-butyl carbazole as the electron donor to synthesize two pure organic luminescent materials, DNBuCz-DCNPy and DNBuCz-Q. By employing conventional chemical synthesis techniques such as nucleophilic substitution, Friedel-Crafts alkylation, and nucleophilic addition-elimination, we produced these materials cost-effectively. We explored the use of varying volume ratios of water and acetone as solvents, and our findings indicated that the luminescent intensity of both materials increased with higher water content, thereby elucidating the phenomenon of AIE enhancement. The development and investigation of these materials could facilitate the application of affordable AIE materials in various domains, including biology, fingerprint detection, and electroluminescence.

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References

[1] Tu, L. Xie, Y. Li, Z. Tang, B. Z. (2021) Aggregation-induced emission: Red and near-infrared organic light-emitting diodes. SmartMat, 2, 326-346.

[2] C, Carla. Peixoto, M. Paixão, J. A. Pineiro, M. Melo, J. S. S. (2024) Tuning the AIE Properties of Di-tert-Butyl-diphenyldibenzofulvene Derivatives. J. Phys. Chem. C, 128, 1156-1164.

[3] Zhao, D. You, J. Fu, H. Xue, T. Hao, T. Wang, X. Wang, T. (2020) Photopolymerization with AIE dyes for solid-state luminophores. Polym. Chem, 11, 1589-1596.

[4] Liu, H. Xiong, L.-H. Kwok, R. T. K. He, X. Lam, J. W. Y. Tang, B. Z. (2020) AIE Bioconjugates for Biomedical Applications. Adv. Opt. Mater, 8, 2000162 .

[5] Zhan, R. Pan, Y. Manghnani, P. N. Liu, B. (2017) AIE Polymers: Synthesis, Properties, and Biological Applications. Macromol. Biosci, 17, 1600433.

[6] Shellaiah, M. Sun, K. (2022) Pyrene-Based AIE Active Materials for Bioimaging and Theranostics Applications. Biosensors, 12, 550.

[7] Zhao,Y. Li, Q. Wang, E. Niu, Z. (2022) Wavelength-tunable AIEgens based on 6-methoxy-2-naphthaldehyde: AIE behavior and bioimaging performance. Spectrochim. Acta. A Mol. Biomol. Spectrosc, 281, 121621.

[8] Hu, R. Yang, X. Qin, A. Tang, B. Z. (2021) AIE polymers in sensing, imaging and theranostic applications. Mater. Chem. Front, 5, 4073-4088.

[9] Hu, L. Sun, Ji. Han, J. Duan, Y. Han, T. (2017) An AIE luminogen as a multi-channel sensor for ethanol. Sens. Actuators B Chem, 239, 467-473.

[10] Zhang, E. Hou, X. Zhang, Z. Zhang, Y. Wang, J. Yang, H. You, J. Ju, P. (2019) A novel biomass-based reusable AIE material: AIE properties and potential applications in amine/ammonia vapor sensing and information storage. J. Mater. Chem. C, 7, 8404-8411.

[11] Gao, Y. Wei, K. Li, J. Li, Y. Hu, J. (2018) A facile four-armed AIE fluorescent sensor for heparin and protamine.Actuators B Chem, 277, 408-414.

[12] Afrina, A. Swamy, P. C. A. (2024) Symphony of light: AIE and MFC in carbazole-based cyanostilbenes. J. Mater. Chem. C, 12, 1923-1944.

[13] He, Z. Tian, S. Gao, Y. Meng, F. Luo, L. (2021) Luminescent AIE Dots for Anticancer Photodynamic Therapy. Front. Chem, 9, 672917.

[14] Xue, B. Hou, A. Du, Y. Qi, Y. Jiang, H. Zhou, H. Zhou, Z. Chen, H. (2023) AIE donor-dependent photosensitizer for enhance photodynamic antibacterial interface. Surf. Interfaces, 39, 102996.

[15] Zhou, C. Zhang, X. Pan, G. Tian, X. Xiao, S. Liu, H. Zhang, S. Yang, B. (2019) Investigation on excited-state properties and electroluminescence performance of Donor-Acceptor materials based on quinoxaline derivatives. Org. Electron, 75, 105414.

[16] He, Y. Zhang, C. Yan, H. Chai, Y. Zhou, D. (2023) A simple strategy for obtaining aggregation-induced delayed fluorescence material achieving nearly 20% external quantum efficiency for non-doped solution-processed OLEDs. Chem. Eng. J, 476, 146675.

[17] Zhang, K. Shu, J. Chu, W. Liu, X. Xu, B. Jiang, W. (2021) AIE and mechanofluorochromic enhancement properties. Dyes Pigments, 185, 108898.

[18] Lai, Q. Liu, Q. Zhao, K. Shan, C. Wojtas, L. Zheng, Q. Shi, X. Song, Z. (2019) Rational design and synthesis of yellow-light emitting triazole fluorophores with AIE and mechanochromic properties. Chem. Commun, 55, 4603-4606.