Substituent Effect on the Solid-State Photoinduced Luminescence of α-Cyanostilbene Derivatives

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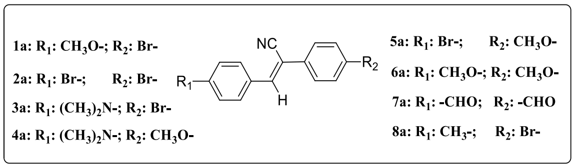
Summary: A series of α-cyanostilbene derivatives with aggregation-induced enhanced emission（AIEE） was obtained. All the compounds were characterized by UV−vis spectroscopy, fluorescence and nuclear magnetic resonance. These compounds exhibited blue, green and yellow color emission in solid state but non-fluorescent in dilute solutions. The electronic characteristics were examined by GAMESS Interface software package. The results indicate that the luminescence properties are affected by the substituents.

Keywords: α-cyanostilbene derivatives, Substituent effect, Solid-state, Luminescence, AIEE.

Introduction

Design and fabrication of efficient light emitters in solid or aggregate state is of importance to the development of advanced optical and biomedical devices. [1-3] **π**-conjugated organic luminophores are one of the essential for modern optoelectronics. Their luminescence is often weakened or even quenched at high concentrations, which is widely known as the aggregation-caused quenching (ACQ).[4, 5] However, it has been reported that the isolated species of α-cyanostilbene derivatives are virtually non-fluorescent in dilute solutions, but show strong fluorescent emission in solid state. [6-9] Such an unprecedented result of aggregation-induced enhanced emission has a significant impact on the design of emissive organic materials, [10-15] which is of great practical importance because of its favorable solid state application prospect, particularly in optoelectronic devices.[16, 17] Affected by its intriguing phenomenon and potential application prospect, many different α-cyanostilbene derivatives have been subsequently developed [18-20]. Moreover, another feasible approach to control the molecular packing arrangements is to tune the packing style of molecules, as the emission of organic solids strongly depends on their packing modes in solid state. [21-23].

Obviously, the substituent groups could control the molecular packing arrangements that change the AIEE properties. In this report, a series of α-cyanostilbene derivatives with different substituents were synthesized and characterized (Scheme-1). The optical properties were studied by UV-vis and fluorescence spectra. The electronic characteristics were examined by GAMESS Interface software package.



Scheme-1: α-cyanostilbene derivatives.

Experimental

Reagents and Apparatus

Unless otherwise stated, all solvents and reagents were commercially available and used without further purification. The ^{1}H-NMR and ^{13}C-NMR spectra ($CDCl_3$) were performed on a Bruker Avance II 400 spectrometer, and using tetramethylsilane as internal standard. The UV-vis spectra were obtained using an Agilent Technologies Carry-60 spectrophotometer. The fluorescence experiments were conducted on a PTI QM40 Fluorescence spectrophotometer with a 1 cm quartz cell.

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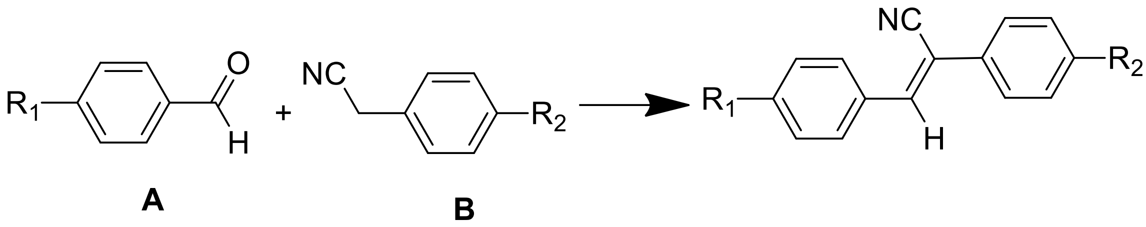

1a: R_1: CH_3O-; R_2: Br-
2a: R_1: Br-; R_2: Br-
3a: R_1: $(CH_3)_2N$-; R_2: Br-
4a: R_1: $(CH_3)_2N$-; R_2: CH_3O-
5a: R_1: Br-; R_2: CH_3O-
6a: R_1: CH_3O-; R_2: CH_3O-
7a: R_1: -CHO; R_2: -CHO
8a: R_1: CH_3-; R_2: Br-

Scheme-2: Synthetic route of compounds **1a-8a.**

Synthesis of compounds 1a-8a

The synthetic procedure is shown in the Scheme-2. To a solution of compound A (0.5 mmol) and compound B (0.5 mmol) in 50 mL of anhydrous ethanol, a solution of sodium methoxide (25 wt%) was added dropwise with vigorous stirring. Upon completion of the addition, the mixture turned cloudy and the suspension was stirred for another 2 h at room temperature and subsequently cooled, precipitates were formed and filtered out. The crude product was recrystallized from ethanol to obtain the title compound.

(Z)-2-(4-bromophenyl)-3-(4-methoxyphenyl)acrylonitrile (**1a**): Light yellow powder, Yield: 80%, m.p.: 124-125 ℃. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.8 Hz, 2H), 7.60-7.48 (m, 4H), 7.44 (s, 1H), 6.99(d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 161.65, 142.24, 133.84, 132.16, 131.34, 127.26, 126.22, 122.85, 118.21, 114.48, 107.44, 55.50. Anal. Calcd for $C_{16}H_{12}BrNO$: C, 61.17; H, 3.85; N, 4.46. Found: C, 61.42; H, 3.88; N, 4.52.

(Z)-2,3-bis(4-bromophenyl)acrylonitrile (**2a**): White powder, Yield: 82%, m.p.: 120-122 ℃. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.5 Hz, 2H), 7.62 – 7.55 (m, 4H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.45 (s, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 141.09, 133.11, 132.34, 132.29, 130.70, 127.49, 125.24, 123.76, 117.39, 111.30. Anal. Calcd for $C_{15}H_9Br_2N$: C, 49.62; H, 2.50; N, 3.86. Found: C, 49.93; H, 2.51; N, 3.89.

(Z)-2-(4-bromophenyl)-3-(4-(dimethylamino)phenyl)acrylonitrile (**3a**): Yellow powder, Yield: 75%, m.p.: 190-192 ℃. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.9 Hz, 2H), 7.50 (q, *J* = 8.6 Hz, 4H), 7.38 (s, 1H), 6.71 (d, *J* = 7.5 Hz, 2H), 3.06 (s, 6H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 151.83, 142.86, 134.63, 131.99, 131.46, 126.92, 121.84, 121.26, 119.16, 111.61, 103.14, 40.07. Anal. Calcd for $C_{17}H_{15}BrN_2$: C, 62.40; H, 4.62; N,8.56. Found: C, 62.28; H, 4.69; N, 8.51.

(Z)-3-(4-(dimethylamino)phenyl)-2-(4-methoxyphenyl)acrylonitrile (**4a**): Orange powder, Yield: 78%, m.p.: 149-150 ℃. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.9 Hz, 2H), 7.55 (d, *J* = 8.9 Hz, 2H), 7.29 (s, 1H), 6.93 (d, *J* = 8.9 Hz, 2H), 6.71 (d, *J* = 9.0 Hz, 2H), 3.83 (s, 3H), 3.04 (s, 6H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 159.57, 151.43, 140.82, 130.97, 128.14, 126.75, 121.85, 119.61, 114.30, 111.65, 104.38, 55.44, 40.11. Anal. Calcd for $C_{17}H_{15}BrN_2$: C, 77.67; H, 6.52; N,10.06. Found: C, 77.25; H, 6.63; N, 9.88.

(Z)-3-(4-bromophenyl)-2-(4-methoxyphenyl)acrylonitrile (**5a**): Light yellow powder, Yield: 85%, m.p.: 139-141 ℃. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.58 (t, *J* = 9.2 Hz, 4H), 7.34 (s, 1H), 6.95 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 160.63, 138.54, 132.85, 132.16, 130.46, 127.38, 126.60, 124.37, 117.93, 114.52, 111.96, 55.50. Anal. Calcd for $C_{16}H_{12}BrNO$: C, 61.17; H, 3.85; N, 4.46. Found:

C, 60.97; H, 3.92; N, 4.38.

(Z)-2,3-bis(4-methoxyphenyl)acrylonitrile (**6a**): Light yellow powder, Yield: 80%, m.p.: 106-107 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 6.8 Hz, 2H), 7.35 (s, 1H), 7.00 – 6.90 (m, 4H), 3.86 (s, 3H), 3.84 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 161.09, 160.11, 139.96, 130.91, 127.36, 127.09, 126.76, 118.72, 114.40, 114.34, 108.34, 55.45, 40.99. Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 77.35; H, 5.81; N, 5.33.

(Z)-2,3-bis(4-formylphenyl)acrylonitrile (**7a**): Yellow powder, Yield: 70%, m.p.: 173-174 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.09 (d, *J* = 4.7 Hz, 2H), 8.08 (d, *J* = 8.2 Hz, 2H), 8.04 – 7.98 (m, 4H), 7.89 (d, *J* = 8.3 Hz, 2H), 7.72 (s, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 191.26, 191.20, 142.70, 139.30, 138.52, 137.52, 136.92, 130.46, 130.21, 130.06, 126.84, 116.91, 113.62, 77.38, 77.07, 76.75. Anal. Calcd for $C_{17}H_{11}NO_2$: C, 78.15; H, 4.24; N, 5.36. Found: C, 77.03; H, 4.38; N, 5.18.

(Z)-2-(4-bromophenyl)-3-(p-tolyl)acrylonitrile (**8a**): White powder, Yield: 73%, m.p.: 108-109°C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.5 Hz, 2H), 7.57 (dd, *J* = 17.0, 8.4 Hz, 4H), 7.41 (s, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 2.39 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 139.77, 139.68, 132.75, 132.20, 131.33, 130.58, 129.85, 125.89, 124.62, 117.87, 112.39, 77.37, 77.05, 76.74, 21.29. Anal. Calcd for $C_{16}H_{12}BrN$: C, 64.45; H, 4.06; N, 4.70. Found: C, 64.57; H, 4.16; N, 4.81.

Result and Discussion

As shown in Fig. 1, the λmax of α-cyanostilbene derivatives shifts from 326 nm to 405 nm. Compound 3a exhibits the largest absorption wavelength, which can be attributed to the extension of **π**-conjugation and the enhanced electron-accepting property.

To examine the aggregating behavior of the α-cyanostilbene derivatives with different substituents, fluorescence spectra and photo of compounds **1a**−**8a** under 365 nm UV light in solid state were evaluated. Compounds 1a−2a and 5a-8a all showed blue emission characteristics with emission maxima in the range of 422−483 nm, whereas 3a showed green emission with maxima at 358 nm and 4a showed yellow emission with maxima at 523 nm respectively. In comparison to the emission spectra of 1a−8a in solid state, the solid-state emission data indicated that it exist AIEE in solid state. The photo exhibited blue (422−483 nm), yellow (358 nm) and green (523 nm) fluorescence, respectively. The red shift in the solid-state spectra is attributed to the different substituents of compounds 1a-8a.

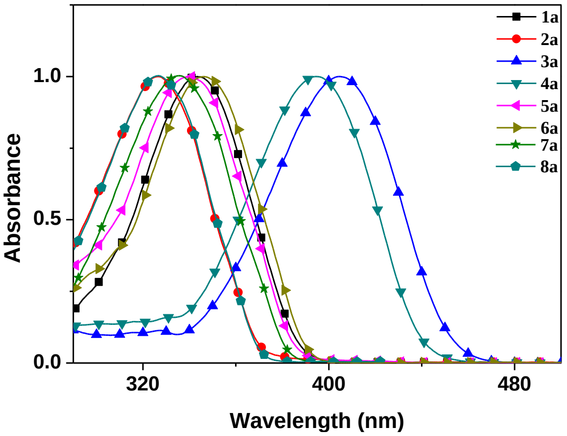

Fig. 1: UV−vis absorption spectra of α-cyanostilbene derivatives in THF(10^{-5} mol/L).

To gain a better understanding of the optical properties and substitution effect of compounds 1a-8a, we performed theoretical calculations on their energy levels by using the GAMESS Interface software package. The simulation results including the optimized molecular configuration, energy levels, and electron distributions of the HOMO and LUMO of these compounds are shown in Table 1 and Figure 3. Among these compounds, compound 1a possesses the highest energy band gap (6.240 eV) while 3a, 4a have relatively smaller energy gaps (5.237 and 5.311eV, respectively). The total order of energy band gaps is ΔE1a > ΔE6a > ΔE5a> ΔE8a > ΔE2a> ΔE4a > ΔE3a> ΔE7a. This result suggests that the band gaps could be tuned by varying the kind of substituents.

Table-1: HOMO and LUMO Energy Levels for α-cyanostibene derivatives.

compound	HOMO(eV)	LUMO(eV)	Eop(eV)
1a	-10.388	-4.640	6.240
2a	-10.207	-4.646	5.561
3a	-9.034	-3.797	5.237
4a	-9.103	-3.792	5.311
5a	-10.642	-4.797	5.845
6a	-10.682	-4.643	6.039
7a	-11.730	-6.974	4.756
8a	-10.625	-4.885	5.740

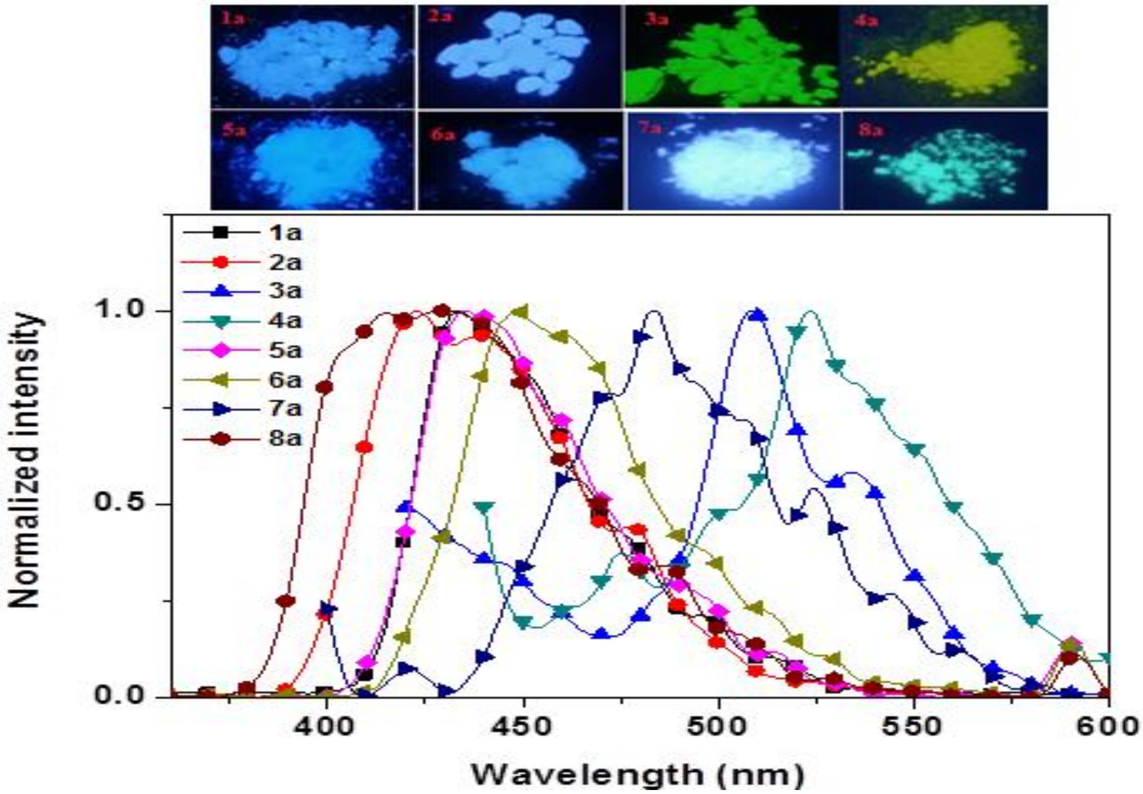

Fig. 2: Fluorescence spectra and photo of α-cyanostilbene derivatives under 365 nm UV light in solid state.

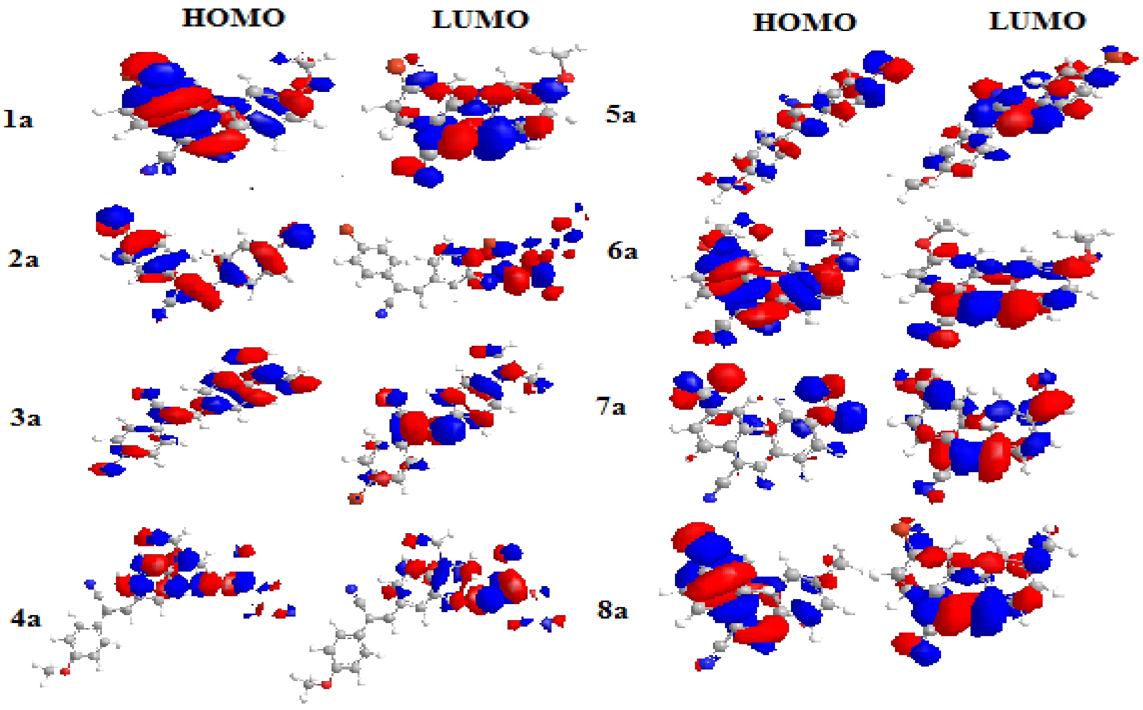

Fig. 3: HOMO and LUMO levels of compounds **1a−8a**.

Although these compounds possessed the same main conjugated backbone, the electron density of the HOMO of 3a is mainly distributed on one side of the whole skeleton but the LUMO prefers to locate on the double-bond group due to the existence of ending bromo and *N*, *N*-dimethyl groups. Similarly, the electron density of the HOMO and LUMO of 7a is attributed to the ending electron withdrawing groups. Therefore, 4a displays the largest red shift because of the ending electron donating groups. The results revealed that the electronic structure of compounds 1a-8a is affected by the ending groups.

Conclusion/Acknowledgements

In summary, we have synthesized and characterized a series of α-cyanostilbene derivatives with different substituents. The effect of substitution groups on the solid-state photo-induced luminescence was studied by UV-vis and fluorescence spectra. The electronic characteristics were examined by the GAMESS Interface software package. The results showed that the substitution groups deeply affect the photo-induced luminescence properties.

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