Substituent Effects of AIE-Active \(\alpha\)-Cyanostilbene-Containing Triphenylamine Derivatives on Electrofluorochromic Behaviors

Sin-Yu Chen, Ya-Wen Chiu and Guey-Sheng Liou

Four AIE- and electro-active cyanostilbene-based triphenylamine-containing derivatives with different substituents were synthesized successfully for investigating the effects on photoluminescent properties, electrochromic (EC) and electrofluorochromic (EFC) behaviors of gel-type electrochromic devices (ECDs). The optical and photoluminescent properties of the obtained materials can be influenced by the substituents, and reveal AIE-active characteristic, exhibiting stronger fluorescence intensity in the aggregated state than in the solution state. Consequently, the electrofluorochromic (EFC) devices could be fabricated by combining these AIE- and electro-active materials with cathodic EC heptyl viologen (HV) into the gel-type electrolyte system for enhancing emission intensity, on/off contrast ratio, and response capability.

Introduction

Organic materials with efficient emission in solid-state are necessary for optoelectronic devices, inclusive of organic light-emitting diodes (OLEDs), organic light-emitting field-effect transistors (OLEFETs) and organic fluorescent sensors. Therefore, the innovation in novel luminescent materials emitting fluorescence in solid state with high efficiency is the main objective for scientists and is strongly expected for realization, modification and further applications of such kind of optoelectronic devices with superior performance. Nevertheless, most organic fluorophores are strongly emissive in the solution state but faintly emissive in the solid state on account of notorious concentration quenching resulted from intermolecular interactions like energy transfer in the aggregated state and excimer formation. Recently, a phenomenon opposite to the traditional aggregation-caused quenching (ACQ) has been discovered and published that a silole derivative emits weak fluorescence in the solution but gradually emits light as the poor solvent increasing in the aggregated state, and the aggregated state is also accompanied by a red shift in the fluorescence spectrum. Such condition is called aggregation-induced emission (AIE), which molecules can perform highly emissive in the aggregated state such as nanoparticle aggregate formations, thin films, powders and crystals to facilitate more optoelectronic applications.

Bifunctional fluorescent molecular switches were first fabricated by Lehn et al. From then on, electrofluorochromic (EFC) devices have been prepared with different electroactive fluorophores, including small organic molecules, inorganic materials, and high-performance polymers. Electrofluorochromism is a phenomenon usually associated with electrochromism (EC) of electroactive fluorophores during redox reaction. Kim and Audebert first prepared EFC device by blending tetrazine derivative with polymer electrolyte. Our group also fabricated the flexible devices performing excellent switching ability from fluorescence neutral state to non-fluorescent monocation radical state with high contrast ratios and low applied potentials by using electroactive polymer films with aggregation-enhanced emission (AEE) effect. Triphenylamine (TPA) has many advantageous features such as good solubility, photoluminescence and EC behavior, while it shows ACQ effect which is a drawback for practical applications. According to the literature reported by Tang’s group, ACQ gens would change to AIE-gens by incorporating AIE fluorophores into the ACQ structures. This kind of approach is facile and effective to obtain AIE-gens. Moreover, cyanostilbene moiety has been frequently utilized as a functional unit in the design of advanced optical materials because of its simple structure and high polarizability. The resulted derivatives display AIE feature because the cyano group can provide not only steric effect to prevent close \(\pi\)-\(\pi\) stacking but also intermolecular hydrogen bonding to rigidify molecules.

Hence, electroactive TPA with ACQ effect is designed to be combined with AIE-active cyanostilbene in this research so as to obtain a series of AIE molecules with highly emissive characteristic in the solid state. In addition, gel-type electrolyte system could be applied to limit the intramolecular motion of AIE molecules for obtaining EFC devices with strong fluorescence. Further, the cathodic EC material of heptyl viologen (HV) could be introduced to act as the counterion-reservoir role for both shortening EC switching time and enhancing contrast ratio of the EFC devices.
Experimental Section

Materials

Commercially available diphenylamine (Alfa), 4-bromobenzaldehyde (AK Scientific), phenylacetonitrile (ACROS), 4-bromophenacylanionitrite (Alfa), p-anisidine (ACROS), 4-bromoanisole (Alfa) and other reagents were used as received. The cathodic EC material heptyl viologen tetrafluoroborate HV(BF₄)₂ was prepared as the follows: 4,4'-dipyridyl (3.12 g, 20 mmol) and 1-bromohexane (31.4 mL, 200 mmol) was added into 30 mL of acetonitrile and refluxed for 6 h, the precipitate was filtered off after cool down to room temperature and washed with organic solvents such as hot chloroform, acetone, hexane, and then dried in vacuum to obtain 96 % in yield of yellow powder HVBr₂ (9.85 g). Afterwards, the solution of HVBr₂ (5.00 g) in DI water (50.0 mL) was dropwisely added to the saturated solution of NaBF₄ (50.0 mL). After 30 min, the white solid HV(BF₄)₂ was obtained after filtration, then purified by recrystallization from ethanol.

Synthesis of triphenylamine-based electroactive materials

Aldehyde derivatives (TPA-CHO and diOMe-TPA-CHO) and phenylacetonitrile (or 4-bromophenacylanionitrite) were used to synthesize the AIE-active α-cyanostilbene-containing triphenylamine luminogens (TPA-CN, diOMe-TPA-CN, TPA-CNB₄ and diOMe-TPA-CNB₄), respectively, by the Knoevenagel condensation as shown in Scheme S1. Take TPA-CN as an instance, a solution of potassium hydroxide (KOH, 0.17 g, 3.0 mmol) in ethanol (10 mL) was added dropwise to the mixture of TPA-CHO (0.55 g, 2.0 mmol) and phenylacetonitrile (0.35 g, 3.0 mmol) in ethanol (10 mL) at room temperature. After stirring for 24 h, clear yellow solid was obtained during the reaction, the resulting crude product was dried to afford a yellow solid (0.65 g, 87%) and purified by recrystallization from ethanol.

Fabrication of gel-type electrofluorochromic device

The procedure to prepare the gel-type electrofluorochromic (EFC) devices is depicted in Figure S1. Two ITO (~5 Ω/square) glasses were confined to a 2 × 2 cm² active area at 120 °C for six hours. A tiny opening was remained for injecting materials into the device through vacuum encapsulating method. The gel-type device contains 0.75 μmole (0.015 M) EFC materials and heptyl viologen (HV), copolymer of methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) (poly(MMA-HEMA), 7.6 mg), aliphatic polyisocyanate (Desmodur® N3200, 6.3 mg) and catalyst dibutyltin diacetate (0.01 mg) dissolving in 0.05 mL propylene carbonate (Figure 1). Once the injection was finished, the opening would be sealed via an UV-curing adhesive, and then was cured at 75 °C for two hours to obtain the crosslinked gel-type EFC device.

Results and discussion

Monomer synthesis and characterization

The synthesis procedure of TPA-based aldehyde derivatives is depicted in Scheme S1. 4-aldehyde-triphenylamine (TPA-CHO) and 4'-aldehyde-4,4'-dimethoxytriphenylamine (diOMe-TPA-CHO) were synthesized according to the previous procedures. 21-22 Then, phenylacetonitriles reacted with aldehyde derivatives to afford 2-(phenyl)-3-[4-(N,N-diphenylamino)phenyl]acrylonitrile (TPA-CN), 2-(phenyl)-3-[4-(methoxyphenylamino)phenyl]acrylonitrile (diOMe-TPA-CN), 2-(4-bromophenyl)-3-[4-(N,N-diphenylamino)phenyl]acrylonitrile (TPA-CNB₄) and 2-(4-bromophenyl)-3-[4-(N,N-diphenylamino)phenyl]acrylonitrile (diOMe-TPA-CNB₄) with yields above 75%.21-24 All compounds were purified by recrystallization and well characterized by nuclear magnetic resonance (NMR) spectroscopy. Besides, the structure of new compound diOMe-TPA-CN was further identified by 2D 1H-1H COSY and 2D 1H-13C HSQC NMR spectra (Figure S2 to Figure S5) and elemental analyses.

Optical properties

The optical properties of the α-cyanostilbene-containing TPA derivatives were investigated by UV-vis spectrophotometer and photoluminescence (PL) spectroscopy. The UV-Vis absorption and PL emission spectra of all chromogens in the DMSO solution and solid state are depicted in Figure 2. The compounds with the bromide and dimethoxy auxochromes exhibit bathochromic effect not only on the maximum absorption peaks (λₘₐₓ) but also maximum emission peaks (λₑₘᵢₓ) both in DMSO solution and solid state. Since incorporating bromide and dimethoxy groups into structure of the materials would endow stronger donor-acceptor ability, resulting in enhanced red-shift behavior. The photos taken under UV illumination also show the consistency with the results mentioned above, and the whole optical characteristics are listed in Table 1.

Photoluminescent properties

The photoluminescent behavior was evaluated at a concentration of 10 μM of prepared compounds in various
diOMe-TPA-CNBr appeared at 599 nm with 0.10% photoluminescence (PL) quantum yield (Φ) in pure DMSO solution estimated by quinine sulfate as standard (Φ₉ = 0.546 dissolved in 1 N H₂SO₄ in 10 μM concentration), indicating the weak emitting ability in dilute solution state. When the poor solvent (water) was added in the solution increasingly before f_w achieving 50%, the PL intensity of diOMe-TPA-CNBr was almost consistent with the condition of pure solution, and the other materials also exhibited the similar PL behaviour as shown in Figure S6 to Figure S8. Among the four compounds, the Φ values (Φ(sol)/Φ(solution)) of diOMe-TPA-CNBr and diOMe-TPA-CN could be massively enhanced (diOMe-TPA-CNBr = 710, diOMe-TPA-CN = 220) when compared to the ones without dimethoxy groups (TPA-CNBr = 19.8, TPA-CN = 9.3). Furthermore, by introducing dimethoxy groups into molecular structures, the stronger donor-acceptor effect brings about both absorption and emission peaks to the longer wavelength that is an additional benefit for tuning the color of emitting light.

To further understand the photophysical properties of these luminogens at solid state, their molecular conformations and packing models in single crystals were demonstrated and the results are illustrated in Figure 4 and Table S1 to S3. The π-π interaction could occur as the face-to-face distance between two molecular planes is smaller than 3.5 Å. In other words, fluorescence quenching will happen when the face-to-face distance of two planes is smaller than 3.5 Å, which is so-called...
According to the results depicted in Figure 4, the shortest inter-planar distances between α-cyanostilbene units in TPA-CN, diOMe-TPA-CN and diOMe-TPA-CNBr are 6.689, 4.941 and 4.096 Å, respectively, indicating all structures beyond limited distance for the formation of π-π interaction (3.5 Å). Hence, these three structures exhibit the AIE properties. Moreover, the shortest distance of C-H...π interactions could be found in the structure of diOMe-TPA-CNBr, which brings out the highest PL quantum yield at solid-state and AIE characteristic $\sigma_{\text{AIE}}$ value.

Electrochemical stability of the materials

For fabricating electrochemically stable electrofluorochromic (EFC) devices, electrochemical stability of these four electroactive materials should be confirmed firstly by repetitive cyclic voltammetry (CV). TPA derivatives without any protecting groups at the para-position of phenyl rings are not so stable under redox reaction according to the literatures.\textsuperscript{25-26} Thus, the molecular structures (TPA-CN and TPA-CNBr) without dimethoxy protecting groups exhibited different CV behaviors compared to the first cycle in the aspect of smaller electric current intensity and the lower $E_{\text{onset}}$ of the following CV curves as illustrated in Figure 5a and 5b. The lower $E_{\text{onset}}$ could be ascribed to the certain extent formation of dimer structure of the benzidine, which comes from the dimerization of TPA$^+$ during the oxidation process, with higher oxidation stability and the lower oxidation potential.\textsuperscript{27} Meanwhile, diOMe-TPA-CN and diOMe-TPA-CNBr with dimethoxy groups exhibit lower oxidation potentials and highly electrochemical stability depicted in Figure 5c and 5d due to the electron-donating capability of dimethoxy groups.\textsuperscript{28} Therefore, in the following EFC device preparation, diOMe-TPA-CN and diOMe-TPA-CNBr were chosen to fabricate and then to discuss EFC behaviors of the obtained devices.

Electrochemical properties of gel-type electrofluorochromic (EFC) devices

Cyclic voltammetry was used to measure the electrochemical properties of gel-type EFC devices derived from diOMe-TPA-CN/HV and diOMe-TPA-CNBr/HV. The cation of HV, HV$^+$, could accept the electrons from the TPA units and become HV$^+$ when oxidation occurred. On the other hand, HV$^+$ serves as the electron donor to the TPA$^+$ during the process of reduction. Therefore, HV introduced into the devices serves as an effectual counter-ion reservoir for decreasing the applied potential, rapidly balancing charges during EC switching and even enhancing the EC performance. Consequently, oxidation potentials for these two systems could be fixed at 1.91 V...
Spectroelectrochemical properties of gel-type EFC devices

The electrochromic behaviors of these EFC devices based on diOMe-TPA-CN/HV and diOMe-TPA-CNBr/HV were investigated, and the resulted spectroelectrochemical spectra are displayed in Figure S9. The characteristic absorption peaks could be observed at 517, 606 and 760 nm for diOMe-TPA-CNBr/HV and 520, 606 and 760 nm for diOMe-TPA-CNBr/HV, respectively. The color changes can be defined by the CIELAB coordinates where diOMe-TPA-CN/HV changed from (91.22, -15.47, 95.73) at 0.0 V neutral form to (67.62, -18.37, 53.21) the oxidation state at 1.8 V, and diOMe-TPA-CNBr/HV behaved from (91.07, -15.47, 95.73) at 0.0 V to (67.75, -11.38, 69.13) at 1.8 V.

Electrofluorochromic properties of the gel-type devices

Based on our previous research, the supporting electrolyte could be replaced by HV,29-30 Accordingly, the devices were all prepared without any supporting electrolyte. AIE-active diOMe-TPA-CN and diOMe-TPA-CNBr with high PL quantum yield of 44.3% and 73.6% in solid state, respectively. Therefore, the gel-type EFC devices based on diOMe-TPA-CN and diOMe-TPA-CNBr were fabricated to inhibit and restrict the intramolecular motion of the AIE molecules by producing a fraction of crosslinking moieties for obtaining stronger PL intensity. In addition, because of the electroactive TPA units within these molecular structures, the EFC devices would show obvious optical absorption change during oxidation procedure and the specific absorption peaks also could quench the light emission of fluorophore and then bring about EFC behaviors with higher PL contrast ratios \( \frac{I_{\text{on}}}{I_{\text{off}}} \). The advantages of introducing the cathodic material HV into device are not only shortening the response time (Figure S11) and lowering the applied potential but also adding an extra absorption peak at 606 nm, which was expected to absorb the emission from the fluorophores, since the emission peaks of the EFC materials are close to the characteristic peak of HV.

As shown in Figure 7a and Figure 8a, PL intensity of the gel-type EFC devices based on both diOMe-TPA-CN/HV and diOMe-TPA-CNBr/HV systems decayed with increasing applied oxidation potentials. Upon applying voltages from 0 V to 1.8 V, the PL intensity of gel-type device with diOMe-TPA-CN/HV was reduced and the PL contrast ratio \( \frac{I_{\text{on}}}{I_{\text{off}}} \) was about 6.75 (Figure 7b). Similarly, the PL intensity of gel-type device with diOMe-TPA-CNBr/HV decreased with higher voltage and achieved the PL contrast ratio of 6.76 upon applying voltages between 0 V to 1.8 V (Figure 8b). The fluorescence switching responses for these two systems were performed as illustrated in Figure 7c and 7d and Figure 8c and 8d, demonstrating that diOMe-TPA-CNBr/HV system behaves shorter response time than diOMe-TPA-CN/HV system under their light emission wavelengths. Furthermore, long-term stability and reversibility of the resulted EFC devices were also investigated by measuring the PL intensity as a function of switching cycles shown in Figure 9.

Figure 7 (a) PL spectra as applying voltage between 0 and 1.8 V, (b) applied voltage vs PL intensity and contrast diagram, (c) fluorescence switching response at different step cycle times of 360, 60, 30, 20, and 10 sec, (d) estimation of fluorescence switching time of 0.75 μmole/0.75 μmole diOMe-TPA-CN/HV between 1.8 (on) and -0.1 V (off) monitored at 545 nm \( \lambda_{\text{ex}} = 408 \text{ nm} \), and (e) EFC behavior of gel-type device of 0.75 μmole/0.75 μmole diOMe-TPA-CN/HV.

Figure 8 (a) PL spectra as applying voltage between 0 and 1.8 V, (b) applied voltage vs PL intensity and contrast diagram, (c) fluorescence switching response at different step cycle times of 360, 60, 30, 20, and 10 sec, (d) estimation of fluorescence switching time of 0.75 μmole/0.75 μmole diOMe-TPA-CNBr/HV between 1.8 (on) and -0.1 V (off) monitored at 551 nm \( \lambda_{\text{ex}} = 413 \text{ nm} \), and (e) EFC behavior of gel-type device of 0.75 μmole/0.75 μmole diOMe-TPA-CNBr/HV.

Figure 9 Long-term stability and switching reversibility results of the EFC devices derived from (a) diOMe-TPA-CN/HV and (b) diOMe-TPA-CNBr/HV with a cycle time of 30 sec.
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The recovery of EFC devices of diOMe-TPA-CN/HV and diOMe-TPA-CNBr/HV was 96% and 98% after 100 and 150 cycles, respectively. The higher EFC reversibility for diOMe-TPA-CNBr/HV could be attributed to the shorter EC response time and emission peak at 551 nm, which is closer to the 606 nm characteristic absorption peak from HV, resulting in lower decay when compared with the case of diOMe-TPA-CN.

Concentration effect of heptyl viologen on EFC behaviors

In order to increase PL contrast ratio of the EFC devices, modulating the concentration would be a feasible method. diOMe-TPA-CN/HV system, with the higher solubility (Table S4), was chosen to demonstrate the concentration effect on EFC behavior. Two different concentration ratios of the systems, 0.75 μmole/1.5 μmole diOMe-TPA-CN/HV and 1.5 μmole/1.5 μmole diOMe-TPA-CN/CNBr/HV, were investigated, and their corresponding spectroelectrochemical behaviors are depicted in Figure S10. The absorbance of all peaks for these two systems increases obviously than the original 0.75 μmole/0.75 μmole diOMe-TPA-CN/HV system. In the system of 1.5 μmole diOMe-TPA-CN and 1.5 μmole HV (Figure S10b), the absorbances of all characteristic peaks are higher than those of 0.75 μmole/1.5 μmole diOMe-TPA-CN/HV (Figure S10a) because one diOMe-TPA-CN molecule can match one HV molecule, resulting in more densely color change. Consequently, the EFC behaviors of these two different diOMe-TPA-CN/HV concentrations could be improved owing to the higher absorbance of all characteristic peaks, 517 nm and 606 nm particularly.

Concentration effect of heptyl viologen on EFC behaviors

The concentration of HV is a key factor for tuning the PL contrast ratio and switching time. In the system of 0.75 μmole/1.5 μmole diOMe-TPA-CN/HV, the excessive 0.75 μmole HV can fasten the charge balance during oxidation process. Hence, the coloring time was reduced effectively from 11 s to 3 s while the bleaching time was merely decreased from 21 s to 20 s, which indicates that the process of obtaining electron would scarcely be influenced by electron storage layer. Furthermore, when the concentration of diOMe-TPA-CN was increased to double, the PL contrast ratio could be enhanced obviously from 8.15 to 14.4 with the switching time of 5 s/19 s (coloring time/bleaching time). Although the coloring time of 5 s is longer than 3 s of the 0.75 μmole/1.5 μmole diOMe-TPA-CN/HV system, but still much better than 11 s of the 0.75 μmole/0.75 μmole diOMe-TPA-CN/HV system, which is 6 s shorter in response time. Consequently, by just increasing the concentration of HV or both of EC materials, the resulted EFC devices can effectively shorten the switching times and raise the PL contrast ratio.

Conclusions

Novel electrofluorochromic (EFC) devices could be successfully fabricated by combining aggregation-induced
emission (AIE)-active molecules with gel-type system to achieve stronger emission at neutral state. For the purpose of reducing switching response times and raising the PL contrast ratios of EFC devices, heptyl viologen (HV) was introduced into both diOMe-TPA-CN and diOMe-TPA-CNBr systems to bring about lower working potentials, shorter switching response times and higher PL $I_{on}/I_{off}$ contrast ratios. Furthermore, PL contrast ratio of the EFC devices could be further enhanced by tuning the ratio of electrofluorochromic material and HV in the diOMe-TPA-CN/HV system to acquire not only higher PL contrast ratio of 14.4 but shorter EFC switching response time of 5 s/19 s (coloring time/bleaching time). Accordingly, these results demonstrate that the facile approach of combining AIE-active molecules with gel-type system could readily prepare the novel EFC devices with stronger emission intensity at the neutral state and enhanced EFC behaviors.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was financially supported by the “Advanced Research Center for Green Materials Science and Technology” from The Featured Area Research Center Program within the framework of the Higher Education Sprout Project by the Ministry of Education (107L9006) and the Ministry of Science and Technology in Taiwan (MOST 107-3017-F-002-001 and 107-2113-M-002-002-MY3).

References

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**Keyword:** aggregation-induced emission, electrofluorochromic device, α-cyanostilbene, gel-type

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