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Regulating piezofluorochromism of 9,10-bis(butoxystyryl)anthracenes by isomerization of butyl group

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012Yao Xiong,^{a, b} Xilong Yan,^{a, b} Yawen Ma,^{a, b} Yang Li,^{a, b} Guohui Yin,^{* c} and Ligong Chen^{*a, b}

DOI: 10.1039/x0xx00000x

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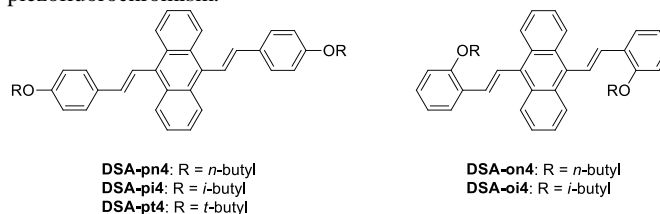
Isomers of 9,10-bis(butoxystyryl)anthracene (DSA₄), including *n*-butyl, *i*-butyl and *t*-butyl at *ortho* or *para* positions, were designed and synthesized. All of them display aggregation-induced emission phenomenon. Remarkably, it was found that isomerization of butyl endgroups presents significant influences on their piezofluorochromic properties. Thus, an alternative approach to design and obtain piezofluorochromic compounds is proposed here.

Piezofluorochromic materials exhibiting variable colors in response to external forces are attracting intensive interest due to their potential applications in optical recording and fluorescence sensors.¹ This scientific trend has been boosted by the finding of aggregation-induced emission (AIE) phenomena (Tang et al, 2001).² Generally, AIE molecules are characterized by strongly twisted conjugation skeletons bearing rotatable aryl moieties,³ which enable them to emit more efficiently in the aggregated or solid state. Since then, AIE materials have been found to be promising stimuli-responsive materials.⁴⁻⁷ As the first piezofluorochromic aggregation-induced emission (PAIE) compound was reported by Park et al. in 2010,⁴ a number of novel PAIE compounds were synthesized and extensively studied.⁸

To date, 9,10-bis(arylvinyl)anthracene derivatives are one of the most popularly investigated categories among PAIE compounds owing to their fundamental importance in understanding the relationship between molecular packing modes and photophysical behaviors.⁹ Based on current researches, it has been demonstrated that the piezofluorochromic (PFC) behaviors of 9,10-bis(arylvinyl)anthracenes could be significantly affected by the peripheral aryl units connected to the 9,10-anthylene core.¹⁰⁻¹³ On one hand, controlling length of linear alkyl chains attached to the peripheral aryl units has been reported as an effective way to tune PFC activities of some AIE compounds, such as 9,10-bis(alkoxystyryl)anthracenes (DSA_n),¹⁰ 9,10-bis[(*N*-alkylphenothiazin-3-yl)vinyl]anthracenes (PT-C_n)¹¹ and 9,10-bis[(*N*-alkylcarbazol-3-yl)vinyl]anthracenes (ACZ_n).¹⁴ On the other hand,

for DSA_n, varying alkoxy-chains' linking positions from *ortho*, *meta* to *para* at peripheral aryl rings has been found to greatly influence their PFC properties.³ However, branched alkyl chains modified AIE compounds including 9,10-bis(alkoxystyryl)anthracenes are rarely reported. Considering that branched alkyl chains would affect molecular backbone conformation and stacking structure, so different PFC properties should be expected.

Herein, five isomers (*n*-butyl, *i*-butyl, and *t*-butyl at *ortho* or *para* positions) of 9,10-bis(butoxystyryl)anthracenes (DSA₄, Scheme 1) were designed and synthesized, their optical properties and PFC performances are intensively investigated. All these DSA₄ are AIE-active, whereas they exhibit obviously different pressing-induced spectral shifts ($\Delta\lambda_{\text{PFC}} = 3\sim 53$ nm), signifying that isomerization of alkyl chains can be chosen as an alternative approach to alter PFC properties of DSA_n compounds. It should be noted that this strategy is of great possibility to regulate other AIE-active compounds' piezofluorochromism.



Scheme 1 Chemical structures of five DSA₄'s isomers

The aggregation-induced emission properties of 9,10-bis(butoxystyryl)anthracenes were firstly examined. By dissolving the isomers in THF aqueous solutions with different water fractions, their photoluminescence (PL) were recorded respectively. It was found that all of them show obvious aggregation-induced emission properties, weak emission in pure THF, whereas enhanced fluorescence with the increase of water fractions. Taking DSA-pt4 as an example (Fig.1), weak emissions were observed until a water fraction of up to 70% was added to the THF solution. As water fraction continues to rise, the PL intensity begins to dramatically increase to its peak at 124.6, which is almost 25.4 times as that in

pure THF solution. This observation clearly demonstrates that **DSA-pt4** is of AIE activity. It can be ascribed to the molecule aggregation with the increase of water fraction, in which the twisted conjugated molecular structure will hamper intramolecular torsion motion and inhibit the non-radiative decay, resulting in higher PL intensity. When water fraction continues to increase to 90%, a PL intensity reduction and a slight red-shifted emission have also been noticed. This phenomenon was commonly observed in the determination of AIE effects, but the reasons remain unclear.¹⁵ Similar AIE behaviors were also observed for the other isomers of **DSA4**. (ESI† Fig. S1)

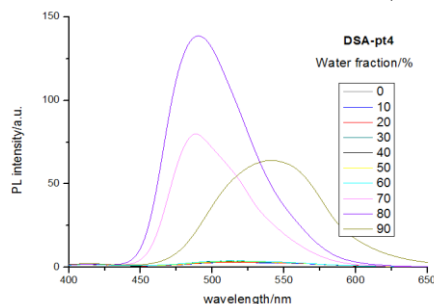


Fig. 1 PL spectra of **DSA-pt4** in different concentrations of THF aqueous solutions

Then, piezofluorochromic behaviors of all the isomers were investigated. As shown in **Fig. 2**, **DSA-pn4** and **DSA-pi4** emit yellow fluorescence in pristine states as prepared, and display slight color changes in ground states, but obvious color changes from green to yellow luminescence before and after grinding were witnessed for **DSA-pt4**, **DSA-on4** and **DSA-oi4**, which illustrated these three isomers are sensitive to external force stimuli with significant color changes. Moreover, the ground samples recovered to green colors after fuming with dichloromethane vapor, and turned yellow again by regrinding. This process is reproducible and can be repeated several times, indicating that **DSA-pt4**, **DSA-on4** and **DSA-oi4** exhibit excellent piezofluorochromic properties.

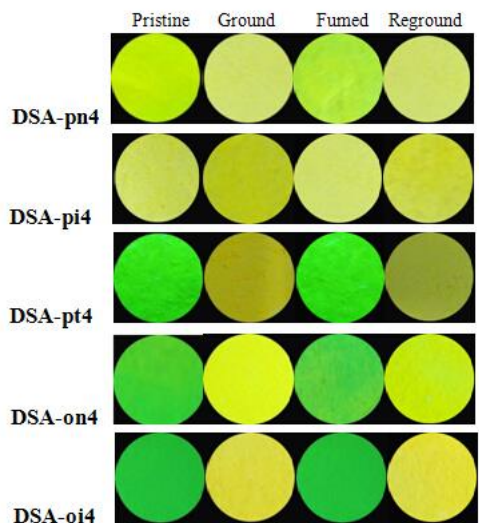


Fig. 2 Fluorescence images of pristine, ground, fumed and reground samples of five **DSA4**'s isomers under a 365 nm UV lamp

Meanwhile, photoluminescence spectra of the five samples in pressed, fumed and repressed states have been conducted to quantitatively investigate their optical properties responding to external forces. The

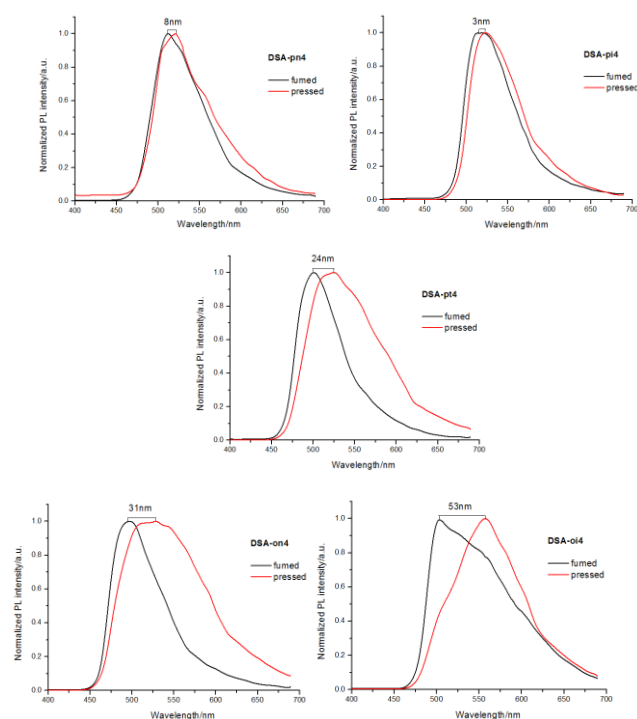


Fig. 3 Fluorescence spectra of **DSA4** in pressed and fumed states

recorded spectra are shown in **Fig. 3** and the corresponding spectroscopic data are summarized in **Table 1**. The pristine solids emit with peak wavelengths of 497–519 nm, in which **DSA-pt4**, **DSA-on4** and **DSA-oi4** present similar emission wavelengths around 500 nm, while the emissions of **DSA-pn4** (512nm) and **DSA-pi4** (519 nm) are more bathochromic. After pressing, **DSA-pn4** and **DSA-pi4** exhibit slight wavelength changes ($\Delta\lambda_{\text{PFC}}$) with only negligible 8 nm and 3 nm compared to the emission wavelengths of samples at original state, respectively. As for **DSA-pt4**, **DSA-on4** and **DSA-oi4**, significant piezofluorochromisms are observed (**DSA-pt4**: $\Delta\lambda_{\text{PFC}} = 24$ nm; **DSA-on4**: $\Delta\lambda_{\text{PFC}} = 31$ nm; **DSA-oi4**: $\Delta\lambda_{\text{PFC}} = 53$ nm). It is further found that pressing exhibits the same effectiveness as grinding, also, **DSA-pt4**, **DSA-on4** and **DSA-oi4** turn out to be more piezofluorochromic. These results, well consistent with the fluorescence color changes observed under an UV-lamp, clearly demonstrate that isomerization of alkyl chains have an remarkable effect on the PFC behaviors of 9,10-bis(alkoxystyryl)anthracenes. Moreover, it's clear that *ortho*-substituted 9,10-bis(butoxystyryl)anthracenes display more prominent piezofluorochromic properties than the *para*-substituted ones. Meanwhile, the pressing-induced spectral shift of **DSA-oi4** increases over 20 nm than that of **DSA-on4** and almost reaches the biggest $\Delta\lambda_{\text{PFC}}$ among all the reported 9,10-bis(alkoxystyryl)anthracenes derivatives, which incline to denote the greater effect of isomerization of alkyl chains on piezofluorochromic properties of *ortho*-substituted **DSA_n**.

Table 1 Peak emission wavelengths (λ /nm) of **DSA4** under various external stimuli

samples	λ pressed/nm	λ fumed/nm	λ repressed/nm	$\Delta\lambda_{\text{PFC}}/\text{nm}$
DSA-pn4	520	512	521	8
DSA-pi4	522	519	524	3
DSA-pt4	524	500	523	24
DSA-on4	528	497	527	31
DSA-oi4	557	504	556	53

Pressing-induced spectral shift, $\Delta\lambda_{\text{PFC}} = \lambda_{\text{pressed}} - \lambda_{\text{fumed}}$

To further understand the mechanism of PFC behaviors displayed by **DSA₄**, wide-angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC) were employed to examine their pristine and ground samples. The WAXD curves of five **DSA₄** (ESI† Fig. S2) present similar sharp peaks before and after grinding, signifying that both of pristine and ground **DSA₄** samples are all in crystalline states. In comparison with the sharp and intense reflections showed by pristine solids, the ground samples display low-intensity reflections along with some peaks missing, indicating the changes in molecular packing structures of crystals and somewhat amorphous features.¹⁴ The remained crystalline features in the ground samples occurring in the WAXD patterns can be probably attributed to the incomplete phase transition. The differences and variations in the crystalline patterns implied that piezofluorochromic properties of **DSA₄** are closely related to the structural changes in molecular aggregation. DSC measurements show that **DSA-pn4** and **DSA-pi4** have two endothermic peaks upon heating (ESI† Fig. S3), while the rest three isomers only have one peak. The peaks in the low-temperature zone for **DSA-pn4** and **DSA-pi4** could be ascribed to the phase transition (T_L) from crystalline to liquid crystal,³ and these T_L peaks become slightly flat and broad after grinding. The high-temperature peak, recognized as the isotropic melt transition (T_H), is found to remain unchanged before and after grinding. It should be noted that phase transition and its change upon grinding are irrelevant to PFC behaviors, **DSA-pt4**, **DSA-on4** and **DSA-oi4** have no phase transition features but exhibit significant PFC properties.

Single crystals with highly ordered molecular packing structures can provide direct and definitive evidence for the relationship between the molecular aggregation state and luminescence properties. By slowly vaporizing petroleum ether into the saturated THF solution of each sample at room temperature, single crystals of **DSA-pn4**, **DSA-pt4**, and **DSA-oi4** suitable for X-ray structural analysis were obtained.

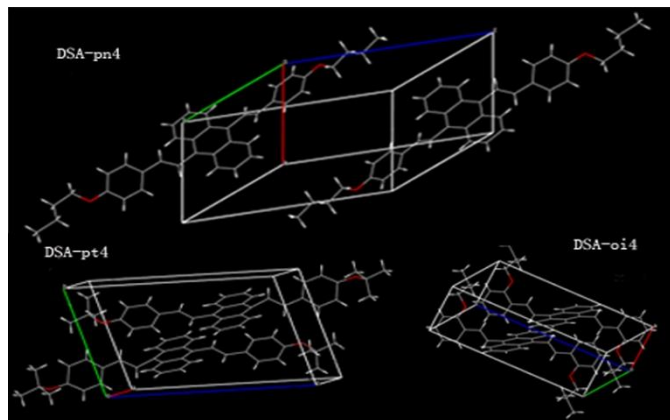


Fig. 4 Stacking modes of **DSA-pn4**, **DSA-pt4** and **DSA-oi4** molecules in crystals

Systematic analysis on X-ray spectra (Fig. 4) revealed that all the isomers' conformations maintained torsion angles between anthracene core and peripheral aryl rings (68.25° for **DSA-pn4**, 73.24° for **DSA-pt4**, and 78.63° for **DSA-oi4**), coinciding with our speculation that the larger dihedral angle (DHA) of the molecule presents the shorter PL wavelength (Table 1). It is easy to understand that larger DHA makes the molecule exist in a more twisted pattern, which could hinder the internal molecular conjugation and lead to induce blue-shifted emission. Moreover, the packing structures of all the crystals are different. In the case of

DSA-pn4, molecules adopt a stacking mode with J-type aggregation along the long axis of the molecule with an inclination angle of 39.54° and there is practically no overlapping between the central anthracene planes, denoting that almost no π - π interaction is formed within **DSA-pn4**. The tight intermolecular packing, indicated by the relatively short vertical distance (3.476 Å) between two close neighbouring molecules, might account for its poor piezofluorochromism ($\Delta\lambda_{PFC} = 8$ nm). As for **DSA-pt4** and **DSA-oi4** crystals, they are assumed to stack with H-type aggregation in view of their inclination angles along the long axis of the molecules (54.87° for **DSA-pt4** and 64.04° for **DSA-oi4**). The vertical distances between two adjacent molecules are 3.637 Å and 3.546 Å for **DSA-pt4** and **DSA-oi4**, respectively. These loose molecular aggregations, rendering the crystals sensitive to external pressure, are thought to result in the significant piezofluorochromism of **DSA-pt4** and **DSA-oi4**.

Conclusions

Five isomers of 9,10-bis(butoxystyryl)anthracene **DSA-pn4**, **DSA-pi4**, **DSA-pt4**, **DSA-on4** and **DSA-oi4** were designed and synthesized. All of them are AIE active, in which, **DSA-oi4** displays the largest PFC spectral shift ($\Delta\lambda_{PFC} = 53$ nm). It was found that bulky branched-chains such as *i*-butyl and *t*-butyl will greatly enhance piezofluorochromism of **DSA₄** with alkoxy chains linked at *para*- and *ortho*-positions of phenyl rings and this isomeric effect of alkyl chains is more influential for the *ortho*-substituted **DSA₄**. Investigation on the relationship between their photophysical properties and the structure of butyl substituted **DSA₄** demonstrated the isomeric effect of alkyl endgroups on **DSA₄**'s piezofluorochromism. Furthermore, X-ray crystallographic analyses clearly reveal that the structures of alkyl chains at peripheral aryl rings of 9,10-bis(arylviny)anthracenes could alter molecular backbone conformations and solid-state packing structure, inducing different optical properties. These findings suggest that isomerization of alkyl chains can be chosen as an alternative way to tune PFC properties of **DSA_n** compounds and this strategy is of great possibility to regulate other AIE-active compounds' piezofluorochromism.

Notes and references

^a School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, P. R. China. Fax: +86-022-27406314; Tel: +86-022-27406314; E-mail: lgchen@tju.edu.cn

^b Collaborative Innovation Centre of Chemical Science and Engineering (Tianjin), Tianjin 300072, P.R. China

^c School of Science, Tianjin University, Tianjin 300072, P. R. China yingh21@aliyun.com

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