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4 **9-Arylvinyl- and 9,10-bis(arylvinyl)-anthracenes with phenyl and naphthyl**
5 **as aryl moieties: Differential aggregation behaviors and optoelectronic**
6 **properties**

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22
23 **ABSTRACT**
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25 In this paper, we have synthesized four simple twisting arylvinyl anthracene
26 derivatives, 9-styrylanthracene (**ASB**), 9,10-bis(styryl)anthracene (**SB**), 9-(2-(naph-
27 thalen-1-yl)vinyl)anthracene (**ASN**) and 9,10-bis((naphthalen-1-yl)vinyl)anthracene
28 (**SN**), to demonstrate the effect of skeleton symmetry on optical and optoelectronic
29 properties. The results showed that **SB** and **SN** are weak emission with the
30 fluorescence quantum yields (Φ) of ca. 7 % but **ASB** and **ASN** are highly fluorescent
31 ($\Phi \approx 50$ %) in THF solution, although they all exhibit high solid-state fluorescence
32 efficiencies (22 ~ 50 %). Grinding could induce about 20 nm of spectral shift of **ASB**
33 and **ASN** crystalline fluorescence, but **SB** and **SN** crystals hardly exhibit mechano-
34 fluorochromic behavior. Furthermore, the evaporated films of **SB** and **SN** are fragile
35 due to re-crystallization soon, but those of **ASB** and **ASN** are stable and could be used
36 as the bulk emissive layer exhibiting commendable electroluminescent performances.
37 This finding indicates that the geometric structures of conjugated skeletons could
38 influence the electronic and aggregate structure of organic luminogens, and then alter
39 their optical and optoelectronic properties.

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41 **Keywords:** 9-Arylanthracene; 9,10-Bis(aryl)anthracene; Geometric effect;
42 *Electroluminescence; Piezofluorochromism.*

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46 **1. Introduction**
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Conjugated organic molecules exhibiting high solution and solid-state fluorescence efficiency are promising materials for the potential applications in fluorescence imaging, chemo-sensing, light emitting diodes, and active gain media for optically pumped solid-state lasers [1–12]. However, common organic chromophores show aggregation- or crystallization-quenched emission (AQE) effect due to strong intermolecular π – π stacking interactions, a typical problem of most fluorescent organic molecules [13,14]. To alleviate or overcome this problem, both the introduction of bulky sterical hindrance groups and the construction of twisted skeleton conformation are effective approaches [15,16]. Since Tang's discovery, conjugated organic molecules with twisted skeletons bearing rotatable aryl moieties have attracted much attention due to their aggregation-induced emission (AIE) or crystallization-enhanced emission (CEE) effects [17–24]. The emergence of these new π -conjugated organic materials has widened the scope of molecular candidates applicable in optics and optoelectronics. 9,10-Bis(arylvinyl)anthracene derivatives are just a class of promising and attractive AIE/CEE molecules, and their AIE behavior was first demonstrated by Prasad et al. in 9,10-bis[4'-(4''-aminostyryl)styryl]-anthracene and used in two-photon fluorescence imaging and photodynamic therapy [25–27]. Recently, there have been a variety of reports on the synthesis and applications of 9,10-bis(arylvinyl)anthracenes[27]. It has been found that most 9,10-divinylanthracene derivatives are not only AIE/CEE active but also piezofluorochromic. 9-Arylvinylanthracenes are also skeleton-twisted dyes; however, their aggregation behavior and optoelectronic properties are rarely investigated. We considered that the geometric symmetry of conjugated skeletons could influence the electronic and aggregate structure of organic luminogens, thus their optical and optoelectronic properties might be tuned or changed by changing substitution patterns. Here we have synthesized four simple anthrylvinyl derivatives, 9-styrylanthracene (**ASB**), 9-(2-(naphthalen-1-yl)vinyl-2)anthracene (**ASN**), 9,10-bis(styryl)anthracene (**SB**), and 9,10-bis-((naphthalen-1-yl)vinyl-2)anthracene (**SN**), to investigate the effect of skeleton symmetry on the optical and optoelectronic properties. We now report that 9-arylvinyl- and 9,10-bis(arylvinyl)-anthracenes exhibit differential optical and optoelectronic properties.

2. Experimental

2.1. Materials

Solvents and reagents were all commercially available analytical-grade products and used as received without further purification, unless otherwise stated. Tetrahydrofuran (THF) was distilled over metallic sodium and dimethyl formamide (DMF) over calcium hydride before use. Anthracene, benzaldehyde, 1-naphthaldehyde, charge-transporting materials, and catalysts were purchased

1 from Aldrich Chemical Co. or Energy Chemical Co., China. 9,10-Bis-
2 (diethoxylphosphorylmethyl)anthracene is from previous work [28].

3 4 2.2. Measurements

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6 ^1H and ^{13}C NMR spectra were recorded on a Bruker AC500 (500/125 MHz)
7 spectrometer using deuterated chloroform (CDCl_3) as solvents and tetramethyl-
8 silane (TMS) as internal standard. UV-vis absorption spectra were recorded on
9 a Hitachi U-4100 spectrophotometer. Fluorescence measurements were carried
10 out with a Hitachi F-4600 spectrophotometer. Solution fluorescence quantum
11 yield (Φ) was determined at room temperature by the relative dilution method
12 using quinine (in 0.1 M H_2SO_4) as the reference [28]. Solid-state fluorescence
13 efficiencies were measured on an integrating sphere (C-701, Labsphere) with a
14 325 nm Xe light as the excitation source. Cyclic voltammetry (CV) was
15 performed with a BAS 100W Bioanalytical Systems, using a glass carbon disk
16 (diameter = 3 mm) as the working electrode, a platinum wire as the auxiliary
17 electrode with a porous ceramic wick, and Ag/Ag^+ as the reference electrode
18 standardized by the redox couple ferrocenium/ferrocene. All solutions were
19 purged with a nitrogen stream for 10 min before measurement. The procedure
20 was performed at room temperature, and a nitrogen atmosphere was maintained
21 over the solution during measurements. Differential scanning calorimetry
22 (DSC) was performed on a Netzsch DSC204F1 at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$.

23 24 2.3. Device Fabrication

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26 Indium-tin oxide (ITO) coated glass with a sheet resistance of $15\text{--}20\text{ }\Omega/\text{cm}^2$
27 was used as the cathode whose substrate was pre-patterned by photolithography
28 to reserve an effective device size of 6.25 mm^2 . Then, it was cleaned in an
29 ultrasonic bath with acetone, detergent, deionized water, and isopropanol as the
30 clean agent. After being dried in an oven, it is treated with oxygen plasma for 4
31 min, and then 40 nm of PEDOT:PSS layer was spin-coated and baked
32 overnight in a vacuum oven at $80\text{ }^\circ\text{C}$. On the top of above active layer,
33 N,N'-di(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine (NPB) as hole-
34 transporting layer (40 nm), **ASB** (or **ASN**) as bulk emitting layer (EML, 20 nm)
35 and 1,3,5-tri(phenyl-2-benzimidazolyl)benzene (TPBi) as electron-transporting
36 layer (50 nm) were vacuum deposited in a sequence. Finally, 0.5 nm of LiF
37 film and 100 nm of Al film were vacuum deposited to form the anode at a base
38 pressure of $3 \times 10^{-4}\text{ Pa}$. The thickness of each deposition layer was monitored
39 using a quartz crystal thickness/ratio monitor (STM-100/MF, Sycon). Electro-
40 luminescence (EL) spectra were measured by a PR650 fluorescence spectro-
41 photometer. Luminance-voltage and current density-voltage characteristics
42 were recorded simultaneously by combining the spectrometer with a Keithley
43 model 2400 programmable voltage-current source. All measurements were
44 carried out at room temperature under ambient conditions.

45 46 2.4. Synthesis

2.4.1. Synthesis of 9-anthraldehyde (**1**)

A mixture of anthracene (6.0 g, 35.2 mmol) and phosphorus oxychloride (4 mL, 72 mmol) was heated for 1 h at 90 °C, and DMF (4 mL, 50.6 mmol) was added dropwise over 30 min. The resulting mixture was stirred at 95 °C for 15 h and then cooled to 55 °C. After 40 mL of hot water (60 °C) was added, the mixture was warmed to 65 °C and stirred for 30 min. The pH was adjusted to between 4 and 6 by slowly adding aqueous NaOH under vigorous stirring. The mixture was cooled to 50 °C and laid up for 30 min without stirring. After cooled to room temperature, the filtrate was evaporated under reduced pressure. The resulting dark yellow solid was re-crystallized from acetic acid to give yellow crystals (6.0 g, 82.5% yield). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.56 (t, *J* = 10 Hz, 2H), 7.70 (t, *J* = 7.5 Hz, 2H), 8.09 (d, *J* = 7.5 Hz, 2H), 8.72 (s, 1H), 9.01 (d, *J* = 10 Hz, 2H), 11.55 (s, 1H).

2.4.2. Synthesis of 9-anthracenemethanol (**2**)

9-Anthraldehyde (2.0 g, 9.6 mmol) in absolute ethanol (10 mL) was added slowly a mixture of sodium borohydride (1.0 g, 26.4 mmol, in 10 mL of ethanol) at room temperature. After stirring for 2 h, water (5 mL) was poured into the mixture. After filtration, light yellow solid was obtained. This compound was used for next step without further purification.

2.4.3. Synthesis of 9-bromomethyl anthracene (**3**)

A cold solution (0 °C) of 9-Anthracenemethanol (1.5 g, 27.2 mmol) in toluene (45 mL) was slowly added PBr₃ (0.4 mL, 4.1 mmol). The reaction mixture was stirred for 1 h at 0 °C and then stirred for 1 h at room temperature. The mixture was adjusted to pH = 7 by adding saturated sodium carbonate solution. The organic phase was separated and the aqueous phase was washed three times with toluene, and combined organic phase was dried over MgSO₄ and concentrated under reduced pressure. The crude product was re-crystallized from toluene in refrigerator (−10 °C) to afford yellow crystals (1.15 g, 59.2%). This compound was used for next step without further purification.

2.4.4. Synthesis of 9-diethoxyphosphorylmethylanthracene (**4**)

The mixture of 9-bromomethyl anthracene (5.0 g, 18.5 mmol) and triethylphosphite (10 mL) was gently refluxed overnight. After cooling, the excess triethylphosphite was removed under reduced pressure. The crude product was separated by silica gel column chromatography using ethyl acetate/petroleum ether (8/1) as the eluent. A yellow solid was obtained (1.0 g, 74.3% yield). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 1.07 (t, *J* = 5.00 Hz, 6H), 3.80 (q, 4H), 4.21(s, 1H), 4.25(s, 1H), 7.47 (t, *J* = 6.50 Hz, 2H), 7.56 (t, *J* = 6.50 Hz, 2H), 8.00 (d, *J* = 10.00 Hz, 2H), 8.33 (d, *J* = 10.00 Hz, 2H), 8.41 (s, 1H).

1 2.4.5. Synthesis of 9-styrylanthracene (**ASB**).

2 The solution of 9-diethylphosphorylmethyl- anthracene (0.50 g, 1.52 mmol)
3 and benzaldehyde (0.21 g, 1.98 mmol) in anhydrous THF (20 mL) was added
4 potassium *tert*-butoxide (1.37 g, 12.2 mmol) and stirred at room temperature for
5 8 h. The mixture was added into methanol and the precipitate was collected.
6 The crude product was separated by silica gel column chromatography using
7 petroleum ether as the eluent (0.34 g, 80% yield). ¹H NMR (500 MHz, CDCl₃):
8 δ (ppm) 6.96 (d, *J* = 16.60 Hz, 2H), 7.13 (m, 1H), 7.36 (m, 6H), 7.69 (d, *J* =
9 7.70 Hz, 2H), 7.93 (d, *J* = 16.60 Hz, 1H), 8.02 (d, *J* = 8.55 Hz, 2H), 8.36 (d, *J* =
10 8.75 Hz, 2H), 8.41 (s, 1H); ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 122.33,
11 124.84, 125.14, 125.43, 125.99, 126.44, 126.56, 127.98, 128.66, 128.80, 129.69,
12 131.46, 132.72, 137.26. Anal. Calcd for C₂₂H₁₆: C, 94.25; H, 5.75. Found: C,
13 94.11; H, 5.79.

15 2.4.6. Synthesis of 9-(2-(naphthalen-1-yl)vinyl)anthracene (**ASN**).

16 This compound was synthesized by same procedure for **ASB** except that
17 naphthaldehyde (0.308 g, 1.97 mmol) was used. 0.41 g of product was obtained
18 (82.3% yield). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.51 (m, 6H), 7.62 (t, *J* =
19 7.65 Hz, 1H), 7.76 (d, *J* = 16.25 Hz, 1H), 7.91 (t, *J* = 8.55 Hz, 2H), 7.98 (d, *J* =
20 16.20 Hz, 1H), 8.06 (m, 3H), 8.18 (d, *J* = 8.40 Hz, 1H), 8.46 (s, 2H), 8.48 (s,
21 1H) ; ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 122.37, 123.79, 125.20, 125.59,
22 125.77, 125.98, 126.29, 126.59, 127.86, 128.38, 128.71, 129.79, 131.33, 131.50,
23 132.95, 133.75, 134.78, 135.06. Anal. Calcd for C₂₆H₁₈: C, 94.51; H, 5.49.
24 Found: C₂₆H₁₈: C, 94.39; H, 5.45.

26 2.4.7. Synthesis of 9,10-bis(styryl)anthracene (**SB**)

27 9,10-Bis(diethylphosphorylmethyl)- anthracene (0.30 g, 0.627 mmol) and
28 benzaldehyde (0.15 g, 1.37 mmol) were dissolved in anhydrous THF (20 mL).
29 Potassium *tert*-butoxide (1.12 g, 9.98 mmol) was added and the resulting
30 mixture was stirred at room temperature for 8 h. Methanol was added into the
31 mixture and the precipitate was collected. The crude product was separated by
32 silica gel column chromatography using petroleum ether/dichloro-methane
33 (4/1) as the eluent (0.20 g, 83% yield). ¹H NMR (500 MHz, CDCl₃): δ (ppm)
34 6.95 (d, *J* = 16.55 Hz, 2H), 7.37 (t, *J* = 7.35 Hz, 2H), 7.47 (m, 8H), 7.70 (d, *J* =
35 7.65 Hz, 4H), 7.94 (d, *J* = 16.55 Hz, 2H), 8.40 (m, 4H). Anal. Calcd for C₃₀H₂₂:
36 C, 94.20; H, 5.80. Found: C, 94.28; H, 5.75.

38 2.4.8. Synthesis of 9,10-bis((naphthalen-1-yl)vinyl-2)anthracene (**SN**)

39 This compound was prepared by same procedure for **SB** except that
40 naphthaldehyde (0.308 g, 1.97 mmol) was used. The product was obtained by
41 re-crystallization from chloroform (0.38 g, 75% yield). ¹H NMR (500 MHz,
42 CDCl₃): δ (ppm) 7.54 (m, 8H), 7.65 (t, *J* = 7.65 Hz, 2H), 7.78 (d, *J* = 16.15 Hz,
43 2H), 7.93 (m, 4H), 8.02 (d, *J* = 16.15 Hz, 2H), 8.12 (d, *J* = 7.15 Hz, 2H), 8.20 (d,

$J = 9.20$ Hz, 2H), 8.54 (q, 4H). Anal. Calcd for $C_{38}H_{26}$: C, 94.57; H, 5.43. Found: C, 94.51; H, 5.39.

3. Results and discussion

3.1. Synthesis and characterization

The synthetic routes to four simple anthracene-based luminogens, **ASB**, **ASN**, **SB**, and **SN**, are depicted in Scheme 1. Briefly, the Wittig-Horner reaction between arylaldehydes and 9-diethylphosphorylmethyl- or 9,10-bis(diethoxyl- phosphorylmethyl)-anthracenes was employed, and the target products were characterized by NMR and elemental analysis. It should be noticed that, although the products could be obtained by Heck coupling of arylbromide and arylenes, the present reaction is versatile way due to no use of palladium catalysts, high yields, and easy operation. Moreover, the present 9-diethoxyl- phosphorylmethylantracene has provided a useful intermediate for synthesis of other complicated arylvinylantracenes.

3.2. Solution and solid-state photophysical properties

It is known that 1,4,5,8-positions of anthracene ring have strong repulsion on the aryl and vinyl groups linked at its 9- or 10-positions, which could result in strongly twisted backbone conformations. This should prevent from tight intermolecular stacking and usually render molecular backbone with intramolecular torsion motion that facilitates non-irradiation relaxation pathways. Like most other 9,10-bis(arylvinyl)anthracenes, **SB** and **SN** are also weakly emissive in THF solution with fluorescence quantum yields of 8.5% and 7.0%, respectively. This could be explained in terms of freer intramolecular torsion motion in molecular solution. However, the THF solutions of **ASB** and **ASN** are highly fluorescent with fluorescence quantum yields up to 58.9% and 45.4%, respectively. This implies that molecular backbone symmetry could affect significantly their emission behavior, although they all have intramolecular torsion motion moieties. Fig. 1 shows the absorption and emission spectra of the simple anthracene-based luminogens in THF solution. It is observed that absorption and emission of 9,10-bis(arylvinyl)anthracenes (**SB** and **SN**) are obviously red-shifted than those of 9-arylvinyl-anthracenes (**ASB** and **ASN**), which could be ascribed to the extension of conjugation size. On the other hand, naphthylvinyl- and phenylvinyl-anthracenes show the same absorption spectra, implying that the 1-position linking of naphthalene hardly affect the molecular conjugation degree. However, **ASN** (496 nm) and **SN** (599 nm) exhibit red-shifted emission spectra than **ASB** (466 nm) and **SB** (567 nm), respectively. This implies that the existence of larger amplitude relaxation in

1 the excited state for naphthyl than phenyl dyes, which is consistent with their
2 fluorescence quantum yields.

3 All these simple anthracene-based luminogens are crystalline compounds,
4 and their emission spectra in pristine crystalline states are shown in Fig. 2a. As
5 observed above in solution, the crystalline emission spectra of symmetric
6 compounds **SB** and **SN** (500 nm and 532 nm) are red-shifter than those of
7 mono-substituted **ASB** and **ASN** (460 nm and 470 nm), and naphthylvinyl dyes
8 (**ASN** and **SN**) exhibit bathochromic emission over phenylvinyl ones (**ASB** and
9 **SB**). However, these crystalline emissions are obviously blue-shifted in
10 comparison with the respective emissions in solution (Fig. 1). This
11 phenomenon has been observed in other 9,10-bis(arylvinyl)anthracene
12 derivatives and could be ascribed to the more twisted conformations in
13 crystalline states for stabilizing crystal structure by forming strong
14 supramolecular interactions. [19] It is noted that these crystals are all highly
15 fluorescent, and their fluorescence efficiencies are measured to be 36.3%
16 (**ASB**), 49.8% (**ASN**), 44.1% (**SB**), and 36.7% (**SN**), respectively. Moreover,
17 their evaporated films obtained by vacuum deposition are also highly
18 fluorescent, and the fluorescence efficiencies are 33.5% (**ASB**), 29.2% (**ASN**),
19 25.8% (**SB**), and 22.4% (**SN**), respectively. This indicates that **SB** and **SN** are
20 aggregation-enhanced emission dyes, and **ASB** and **ASN** are highly fluorescent
21 dyes in both solution and solid-state. Fig. 2b shows the emission spectra of
22 evaporated **ASB** and **ASN** films. The evaporated films of **ASB** and **ASN** are
23 blue and bluish-green emission with the peak wavelengths of 470 nm and 492
24 nm, respectively, and their fluorescence colors and film morphologies maintain
25 unchanged in the process of experimental operation. Contrarily, the evaporated
26 **SB** and **SN** films re-crystallize and crack soon after the measurement on
27 fluorescence efficiency, so that the emission spectra could not be recorded.
28 Although the origin for these dichotomies is still unclear at present, this work
29 has demonstrated that the subtle manipulation of backbone symmetry is an
30 available way for filling the gap between aggregation-caused emission and
31 aggregation-induced emission.

32 3.3. *Manchano-stimuli response behavior*

35 Conjugated organic materials exhibiting reversible solid-state fluorescence
36 changes by external force stimuli instead of chemical alteration of the
37 molecular structures have attracted immense interest due to their potential
38 applications. Among them, 9,10-bis(arylvinyl)anthracene derivatives are a
39 important class of mechanofluorochromic (MFC) dyes, but a recent report
40 indicated that simple 9,10-distyrylanthracene (**SB**) has hardly MFC behavior by
41 grinding in a mortar with a pestle [29]. Here we have investigated the MFC
42 behavior of as-synthesized several simple anthracene-based derivatives,
43 including **SB**, by grinding crystal powder on the glass plate with a metal
44 spatula, and their fluorescence images under different external stimuli are

1 shown in Fig. 3. It is found that the fluorescence colors of **SB**, especially **SN**,
2 are obviously changed upon grinding and solvent-fuming over dichloromethane
3 (2 min, at room temperature). Moreover, re-grinding could change again
4 fluorescence color, and the changed color could recover upon annealing
5 (heating 3 min in oven at 200 °C). However, that is not the case for **ASB** and
6 **ASN**, their fluorescence colors hardly change upon external stimuli, indicating
7 that molecular backbone symmetry could affect their morphological stability
8 and stimuli response behavior.

9 The fluorescence color changes above were recorded, and the emission spectra are
10 depicted in Fig. 4. If denoting the peak-wavelength difference between ground and
11 annealed states as the grinding-induced spectral shift ($\Delta\lambda$), the $\Delta\lambda$ values of **SB**, **SN**,
12 **ASB**, and **ASN** are 21, 23, 5, and 8 nm, respectively. Bis-substitution dyes show more
13 remarkable MFC behavior than mono- substitution ones. Fig. 5a is the differential
14 scanning calorimetric curves of pristine crystals and ground solids, which shows that
15 their melt points increase with molecular backbone size, but there is no notable
16 information on aggregation morphological changes induced by grinding. In order to
17 better understand those PFC behaviour, we also have carried out powder wide-angle
18 X-ray diffraction (PWXD) measurements on the pristine and ground solids. PWXD
19 measurements reveal these compounds exhibit different structures of molecular
20 aggregation before and after grinding treatment (Fig. 5b). The diffraction patterns of
21 the pristine samples display sharp and intense reflections, indicative of some
22 crystalline order (Fig. 5b). However, the diffraction patterns of the ground samples
23 show broaden and diffuse peaks, indicating destruction of pristine ordered structures,
24 formation of crystal defects, and appearance of some content amorphous states. The
25 existence of residual crystal seeds in the ground states is probably the reason that the
26 ground states could change rapidly back to pristine states upon annealing or
27 solvent-fuming.

3.4. Electroluminescence

32 Considering that commendable solid-state fluorescence efficiency and good
33 morphological stability of **ASB** and **ASN**, their electroluminescence (EL)
34 performances were investigated. The EL device with the configuration of ITO/
35 PEDOT:PSS (40 nm)/NPB (40 nm)/EML (20 nm)/TPBi (50 nm)/LiF (0.5
36 nm)/Al (100 nm) using **ASB** and **ASN** as emissive material layer (EML) was
37 fabricated. As illustrated in Figure 6, the devices emit blue light at 479 nm and
38 green light at 507 nm when **ASB** and **ASN** are used as EML, respectively. Their
39 turn-on voltages are about 3.3 ~ 3.4 V, a relative low value. Fig. 7 shows the
40 Current density–luminance–voltage and the efficiency–voltage characteristics.
41 The device with **ASB** as EML exhibits maximum luminance, current and power

efficiencies of 3290 cd/m², 1.68 cd/A, 1.32 lm/W, respectively, and that with **ASN** as EML affords the improved EL performance with maximum luminance, current and power efficiencies of 5340 cd/m², 3.67 cd/A and 2.68 lm/W, respectively. These results are fairly commendable because of the simple structures of **ASB** and **ASN** without obvious electron- and hole-transporting moieties, and it already demonstrates the potential applications of mono-substitution 9-arylvinylanthracene derivatives in organic light-emitting diodes. To get further information on light-emitting material **ASB** and **ASN**, their electrochemical behaviors are investigated and the corresponding cyclic voltammograms are shown in Fig. 8a. The reversible oxidative and reductive behaviors are observed and indicate that they have the capability of hole- and electron-transporting. The oxidative and reductive potentials are measured as $E_{ox} = 0.74$ and 0.73 eV and $E_{red} = -2.07$ and -2.02 eV for **ASB** and **ASN**, respectively, implying that they have smaller difference in p-doping than n-doping. Based on the onset oxidative and reductive potentials, their frontier molecular orbital energy levels are estimated to be -5.40 and -5.40 eV (HOMO) and -2.59 , and -2.65 eV (LUMO) for **ASB** and **ASN**, respectively (Fig. 8b). The corresponding band gaps calculated are 2.81 and 2.75 eV, respectively, which are qualitatively consistent with the respective EL spectra (Fig. 6). It should be noted that, since the HOMO energy level of hole-transporting layer NPB is -5.4 eV and the LUMO energy level of electron-transporting layer TPBi is -2.70 eV, hole injection from NPB, especially electron injection from TPBi to light-emitting layer is not very easy. This implies that the incorporation of both hole-transporting and electron-transporting units into the 9-arylvinylanthracenes should improve the EL performances.

4. Conclusions

We have designed and synthesized four simple arylvinyl-anthracene derivatives, **ASB**, **ASN**, **SB**, and **SN** to investigate the symmetry effect of conjugation backbone on the optical and optoelectronic properties. It is found that bis- substitution **SB** and **SN** are aggregation-enhanced emission dyes, and mono- substitution **ASB** and **ASN** emit intensely in both the molecularly dissolved solution and the solid states. Moreover, conjugation backbone symmetry could affect the stimuli response behavior and the morphological stability. **SB** and **SN** exhibit more obvious mechanofluorochromic than **ASB** and **ASN**, but the evaporated films are morphologically unstable and could re-crystallize soon. **ASB** and **ASN** evaporated films exhibit good morphological stability and high fluorescence efficiency could be used as light-emitting layer to afford commendable EL performances. These findings suggest that changing the molecular substitution pattern is an available way for filling the gap between aggregation-caused quenching and aggregation-induced emission, and subtle manipulation of conjugation backbone and aryl group could significantly

alter and tune the optoelectronic properties. What's more, the asymmetry effect of conjugation backbone on the optical and optoelectronic properties will be investigated in next work.

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Scheme 1. Synthetic route and chemical structure of simple anthracene-based luminogens studied in this work.

Fig. 1. Absorption and emission spectra of the simple anthracene-based luminogens in THF solution (1.0×10^{-5} M). The peak wavelength of the lowest energy absorption band is used as the excitation wavelength(ASB/ASN,388nm).

Fig. 2. Emission spectra of the simple anthracene-based luminogens under pristine crystal (a) and evaporated film (b) states. The excitation wavelength is at 400 nm.

Fig. 3. Fluorescence images of the simple anthracene-based luminogens under different external stimuli with illumination of 365 nm UV lamp.

Fig. 4. Emission spectra of the simple anthracene-based luminogens under different external stimuli. The excitation wavelength is at 400 nm.

Fig. 5. (a) DSC curves of the simple anthracene-based luminogens under pristine and ground states. (b) Powder X-ray diffraction patterns at room temperature

Fig. 6. Electroluminescence spectra of the light emitting diodes with **ASB** and **ASN** as the emitting layer.

Fig. 7. (a) Current density–luminance–voltage and (b) the luminous efficiency– power efficiency–voltage characteristics of the ITO/PEDOT:PSS (40 nm)/NPB (40 nm)/EML (20 nm)/TPBi (50 nm)/LiF (0.5 nm)/Al (100 nm).

Fig. 8. (a) Cyclic voltammograms of **ASB** and **ASN** in MeCN with 0.1 M Bu₄NPF₆ as a supporting electrolyte at a scan rate of 100 mV/s. (b) Energy diagram of the device with **ASB** and **ASN** as the emitting layer.