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Synthesis and piezochromic luminescence of aggregation-enhanced emission 9,10-bis(*N*-alkylcarbazol-2-yl-vinyl-2)anthracenes

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ABSTRACT

Aggregation-enhanced emission active 9,10-bis(*N*-alkylcarbazol-2-yl-vinyl-2)anthracenes with changed length of *N*-alkyl chains (methyl, propyl, pentyl, and dodecyl) have been synthesized and their piezofluorochromic properties investigated. The results show that these homologues all exhibit remarkable piezofluorochromism with the pressing-induced spectral shifts of 36–45 nm, but the alkyl lengths do not affect significantly the fluorescence properties. The fluorescence emission changes induced by pressing can be restored by heat-annealing or solvent-fuming and regenerated by repressing. Powder wide-angle X-ray diffraction and differential scanning calorimetric experiments reveal that the transformation between crystalline and amorphous states upon external stimuli is responsible for piezofluorochromic behavior.

1. Introduction

Stimuli-responsive luminescent materials are a class of “smart” fluorophores whose fluorescence emissions change upon external stimuli, including photofluorochromism [1–3], piezo- or mechanofluorochromism (PFC) [4–8], vapofluorochromism [9], thermofluorochromism [10,11], acidifluorochromism [12–14], etc. Among them, PFC materials have recently drawn much attention due to their fundamental importance in understanding the relationship between molecular packing modes and photophysical behaviors and their potential applications in sensors, memory, and security inks fields [7,8,15,16]. While a number of fluorescent organic materials exhibiting PFC behaviors have been synthesized and investigated [17–21], aggregation-induced emission (AIE) fluorophores have been the mainstay of PFC materials. The common structural characteristics of AIE molecules are the strongly twisted conjugated backbones and the high intensity of solid-state fluorescence [22–25], which will not only hinder intermolecular close stacking and intense π–π interaction to render these materials probably easy-destructible solid morphologies that show changed optical and optoelectronic properties but also be advantageous to the observation of PFC phenomenon. Among a variety of AIE molecules, 9,10-bis(arylvinyl)anthracene derivatives are the extensively investigated PFC materials. Since Chi et al. reported first the PFC phenomenon of 9,10-disyryl-anthracene end-capped with other bulky or AIE-active moieties in 2011 [19], most, but not all, 9, 10-bis(arylvinyl)anthracene derivatives have been found to show PFC behavior [26]. However, PFC materials are still at the initial state of investigation and the in-depth understanding of PFC phenomena is limited. For example, 9,10-bis(pyridinylvinyl-2)anthracenes and 9,10-bis(*p*-alkxoystyryl)anthracenes show remarkable PFC behavior, but 9,10-bis(styryl)anthracene and its derivatives with AIE end-groups of triphenylethylene do not exhibit PFC activities [26–28]. Also, 9,10-bis(*p*-alkoxystyryl) anthracenes (**OC*n***), 9,10-bis[(*N*-alkylcarbazol-3-yl)vinyl-2]anthracenes (**ACZ*n***), and 9,10-bis[(9,9-dialkylfluorene-2-yl)vinyl-2]anthracenes (**FLA-C*n***) exhibit different alkyl length-dependent PFC behaviors [29,30]. These studies underline the complexity of structure-property relationship of PFC materials and suggest that there is still a great demand on exploitation of new PFC materials and accumulation of relative structure-

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property knowledge. In this context, PFC materials with simple and comparable structures are very interesting since they are not only advantageous to the investigation of structure-property relationship but also could tune the optical properties. However, such molecular design and PFC investigation is still rare. In the current work, we have designed and synthesized a series of AEE-active 9,10-bis(*N*-alkylcarbazol-2-yl-vinyl-2)anthracenes with different length of *N*-alkyl chains (methyl, propyl, pentyl, and dodecyl) (named **A2C*n***, Scheme 1) to examine their PFC behaviors. We found that these AEE homologues exhibit remarkable pressing-induced spectral shifts ($\Delta\lambda_{PFC}$), but their AEE effect and $\Delta\lambda_{PFC}$ values are hardly *N*-alkyl length-dependent. This is obviously different from their isomers **ACZ*n*** [29], underlining once again the complexity of structure–property relationship of PFC materials and the significant effect of the end-arylenes on the solid-state fluorescence properties of 9,10-bis(arylvinyl)anthracene derivatives.

2. Experimental section

2.1. Measurement

^{1}H and ^{13}C NMR spectra were recorded on a Bruker-AC500 (500 MHz) spectrometer with $CDCl_3$ as solvent and teramethylsilane (TMS) as the internal standard. The elemental analysis was performed on Perkin–Elmer 2400. Fluorescence measurements were carried out with Hitachi F-4600 spectrophotometer. The peak wavelength of the lowest energy absorption band was used as the excitation wavelength for the PL measurement. Powder wide angle X-ray diffraction (WXRD) measurements were performed on a Powder X-ray Diffractometry (INCA Energy, Oxford Instruments), operating at 3 kW. Differential scanning calorimetry (DSC) was performed on a Netzsch DSC204F1 at a heating or a cooling rate of 10 °C/min.

2.2. Piezochromic sample preparation and the recovering experiments

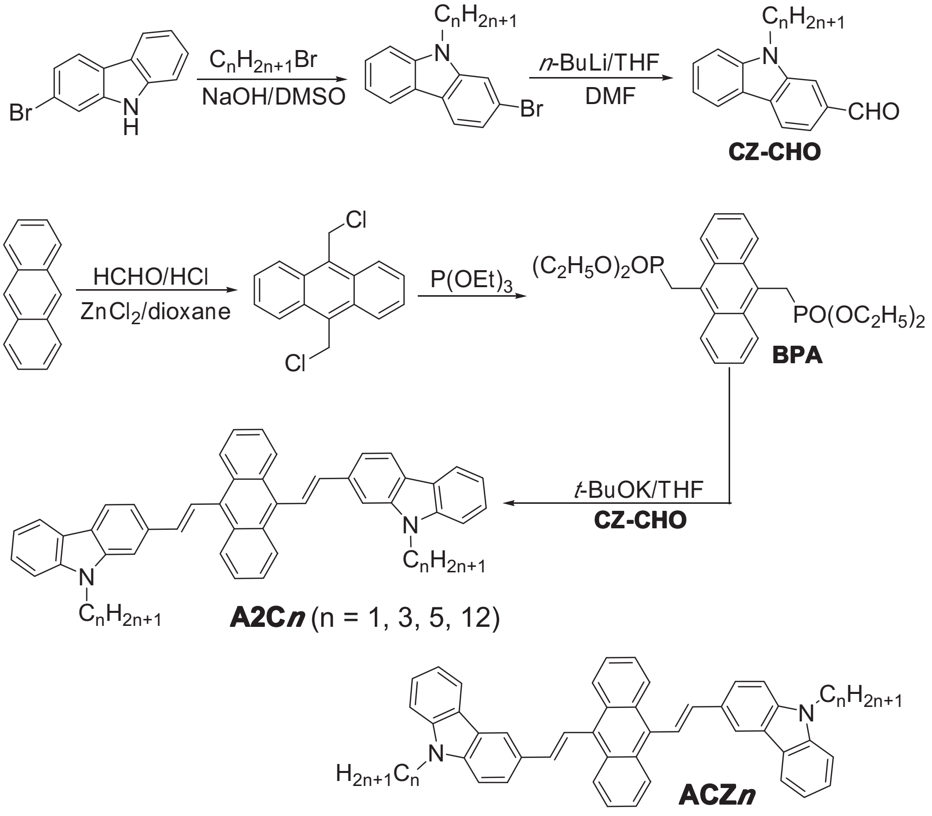
Pressing experiment: A quantity of **A2C*n*** and KBr powder was simply mixed in a mortar and then pressed with IR pellet press for 1 min at room temperature under the pressure of 1500 psi. Annealing experiment: the ground sample was put into an oven with the temperature $T_m - 30$ °C (T_m is the isotropic melt point of each compound) for 3 min. Solvent-fuming experiment: The ground sample was placed above the dichloromethane level and was exposed to the vapor for 1 min at room temperature.

2.3. Synthesis

Synthetic route and structure of 9,10-bis(*N*-alkylcarbazol-2-yl-vinyl-2)anthracenes (**A2C*n***) are shown in Scheme 1. The alkylation of 2-bromocarbazole with *n*-alkylbromide followed by the treatment with $POCl_3$/DMF affords 2-formyl-*N*-alkylcarbazoles (**CZ-CHO**). Chloromethylation of anthracene followed by treating with triethyl phosphite produces 9,10-bis(diethylphosphorylmethyl) anthracene (**BPA**). The target compounds **A2C*n*** are facilely prepared by Wittig condensation between **BPA** and the corresponding **CZ-CHO**, and their structure are characterized by ^{1}H and ^{13}C NMR and elemental analysis.

2.3.1. Synthesis of 9,10-Bis(chloromethyl)anthracene

To a stirred solution of anthracene (1.78 g, 10 mmol), anhydrous $ZnCl_2$ (1.64 g, 12 mmol) and paraformaldehyde (1.50 g, 50 mmol) in dioxane (20 mL) was slowly added concentrated aqueous hydrochloric acid (40 mL) at room temperature. The resulting mixture was gentle refluxed for 3 h and allowed to stand for 16 h at room temperature. The fine granular solid formed was separated by filtration and washed with H_2O and dioxane. The crude product



Scheme 1. Synthetic route and chemical structure of **A2C*n*** homologues. For the sake of comparison, the chemical structure of **A2C*n***'s isomers (**ACZ*n***) is also listed here.