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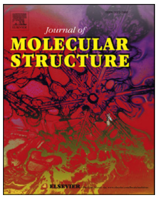

Controlling molecular conformations of alkyl bridged bis-aminostyrene: Investigation of inter-chromophore interaction

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ABSTRACT

A series of bis-aminostyrenes bridged by different aliphatic linkers have been designed and synthesized. Because of tuable molecular conformations, the interactions between two aminostyrene moieties were governed to produce various photophysical and electrochemical properties. When the linkers were ethyl and butyl groups, the behavior of bis-aminostyrene was similar with monomeric aminostyrene. After replacing the linker to be a propyl group, the absorption band became broader and the emission profile displayed significant bathochromic shift. The ethyl and butyl linkers might provide an anti-conformation between two aminostyrenes, and the propyl group might tend to set two aminostyrenes in syn-conformation. Therefore, the relative distance between two pendants might be shorter with propyl group as linker, and thus, inter-chromophore interactions such as exciton coupling take place. These results can be further confirmed by temperature-dependent emission spectroscopy. When the temperature was gradually lowered, the emission spectra of bis-aminostyrenes bridged by ethyl and butyl groups showed bathochromic shift, whereas the propyl substituted one revealed slightly hypsochromic shift. Interestingly, the emission spectrum of propyl substituted bis-aminostyrene was same as that of a monomeric aminostyrene at 150 K, and it could be concluded as destruction of inter-chromophore interaction because of a freeze on molecular motion. On the other hand, a cyclic substituent, piperazine, was chosen to bridge two aminostyrenes, and the chair form of six-member ring forbad inter-chromphore interaction between two aminostyrene. Although, the charge transfer process in aminostyrene was perturbed by piperazine, obvious inter-chromophore interaction would not be observed. These four linkers successfully give the understanding of conformation governing intra-molecular interactions.

1. Introduction

The influence of structure and function represented by the molecules of chemistry and biology is remarkable. Systematic studies on alternative monomers related to those found in nature have provided signs about the fitness of α-amino acids and phosphodiester linkages [1]. Most of the interesting functions carried out by molecules, such as molecular recognition [2], information storage [3], and catalysis [4] that approach conformational uniqueness. These effects were also been observed in polymers and oligomers. Indeed, introduction of alkyl substituents in the flexible spacers of a polymer has been shown to alter the conformation of the polymer [5–7]. Thus, peptide conformations are strongly affected by the presence of C-tetrasubstitution of α-amino acids which can be understood within the framework of Thorpe-Ingold effect [8–11]. Although, the use of a similar strategy to control the conformation of polymers has been explored, the investigation of monomeric conformation which affected photophysical and electrochemical properties is still challenged.

Para-substituted N-alkylanilines (Fig. 1) have been shown remarkable twisted intra-molecular charge transfer (TICT) properties [12]. Different alkyl substituents on nitrogen of aniline derivatives might affect the twisted of structure under photoexcitation, and thus, the charge separation would be altered to perturb the relative intensities between dual emissions coming from local excited state and charge separation state [13].

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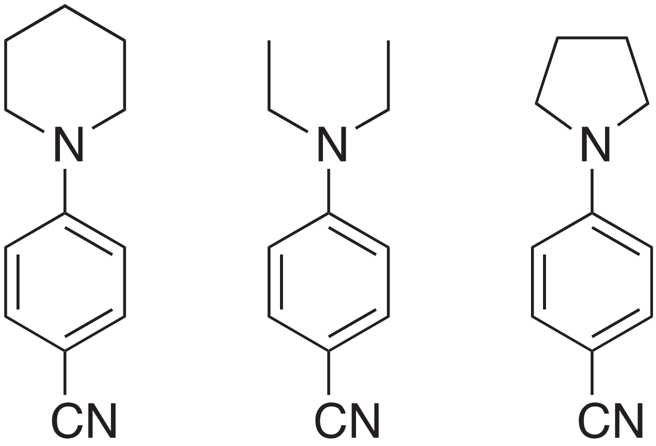


Fig. 1. Para-substituted N-alkylaniline derivatives.

Consequently, the photoinduced charge separation in aniline derivatives was controlled by the geometry of chromophore. An interesting inquiry emerged that the photoinduced charge separation in aniline derivatives would be influenced by inter-chromophore interaction or not. This open question would be investigated via a platform as shown in Fig. 2. A series of alkyl-bridged bis-aminostyrenes were prepared in which four different alkyl linkers were chosen. Aminostyrene has intriguing the study of conducting polymers [14]. Moreover, the vinyl group was terminated by trimethylsilane moiety as an insulator to inhibit unexpected electron transfer and photochemistry processes. It is expected that those model molecules would provide the information about the impact of conformation on TICT.

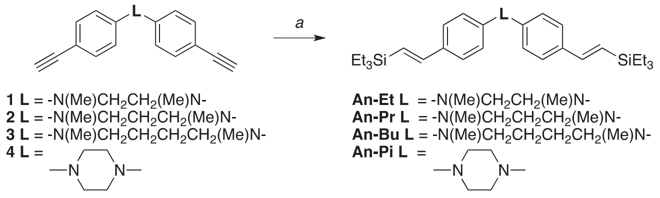
2. Experimental section

2.1. General

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded using a Varian 400 Unity plus (400 MHz) at ambient temperature. Melting point was measured with a Fargo MP-1D melting point apparatus. Infrared spectra (IR) were obtained by using a Thermo Nicolet Avatar 360 E S P. FT-IR spectrometer, and configured with EZ OMNIC software. High resolution mass spectroscopy (HRMS) was obtained using Jeol SX-102A spectrometer. Hitachi U-3900 uv–visible and Hitachi F-7000 fluorescence spectrophotometers were used to acquire the absorption and emission spectra of chromophores. Temperature-dependent fluorescence spectra were measured by using Oxford nitrogen cryostat as sample holder. The temperature was controlled by thermal equilibrium between liquid nitrogen and thermal couple. Methyltetrahydrofuran (MTHF) was employed as solvent due to glass-type phase at low temperature. A CHI potentiostat/galvanostat was used for electrochemical experiments in which Pt electrodes were used to be working and counter electrodes, and Ag/AgCl electrode was used to be reference electrode.

2.2. Synthesis

The synthesis routes of **An-Et**, **An-Pr**, **An-Bu**, and **An-Pi** are shown in Scheme 1. Bis-amines **1**–**4** were prepared based on the corresponding literature [7]. Triethylsilane (SiEt$_3$H) was purchased from Acros, and tris(triphnylphosphine) rhodium(I) chloride was purchased from Aldrich. The reference **An-St** was also prepared according to published report [15]. The experimental details are described below.



[a] SiEt$_3$H, RhCl(PPh$_3$)$_3$ (**An-Et**: 60%, **An-Pr**: 65%, **An-Bu**: 56%, **An-Pi**: 62%)

Scheme 1. Synthesis of bis-aminostyrene derivatives.

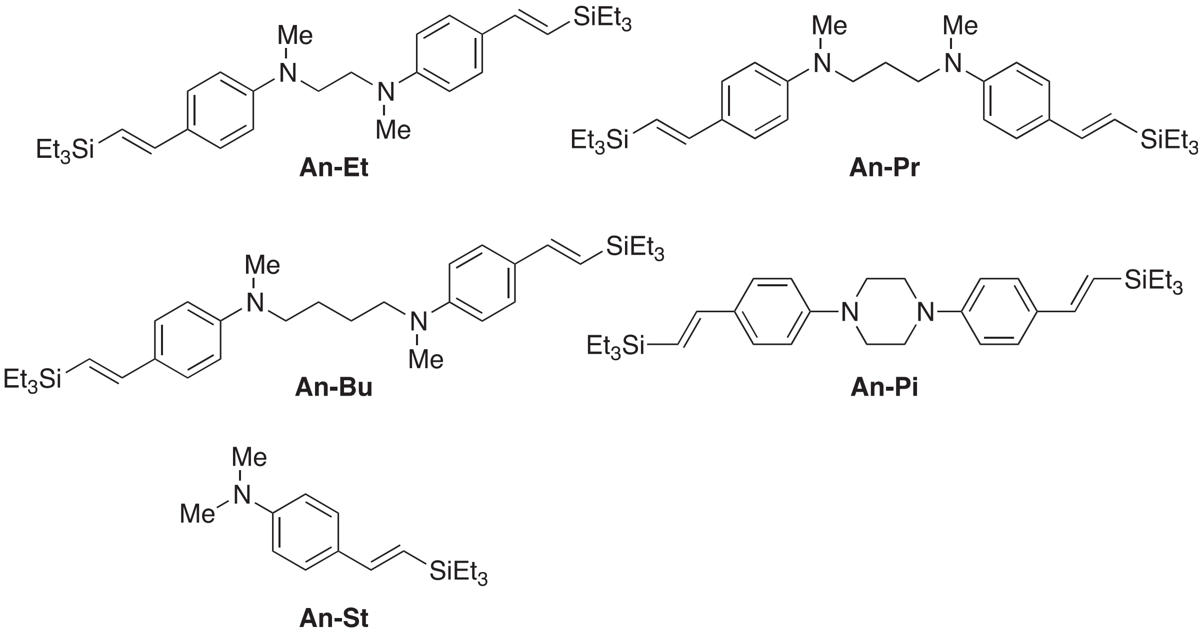


Fig. 2. A series of bis-aminostyrenes terminated by trimethylsilane where **An-St** was utilized as reference compound.