Tetrahedron 74 (2018) 4738–4745

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Substitution position modulating the photophysical properties of anthracene derivatives based on Tröger's base

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ARTICLE INFO

Article history:
Received 8 May 2018
Received in revised form
2 July 2018
Accepted 19 July 2018
Available online 26 July 2018

Keywords:
Positional isomers
Photophysical properties
Anthracene
Tröger's base

ABSTRACT

Three different positional isomers based on Tröger's Base (TB) and anthracene were synthesized by Sonogashira coupling reaction and their optical, structural and electronic properties were compared. It is revealed that changing the substitution position of anthracene units on TB alters the optical and structural properties significantly. All of them are highly emissive in solutions, but when comes to solid state 2,8-*bis*(anthracen-2-ylethynyl)-*6H,12H*-5,11-methanodibenzo[*b,f*][1,5]diazocine (**TBAN2**) shows aggregation-caused quenching quality while 2,8-*bis*(anthracen-9-ylethynyl)-*6H,12H*-5,11-methanodibenzo[*b,f*][1,5]diazocine (**TBAN1**) and 2,8-*bis*(anthracen-1-ylethynyl)-*6H,12H*-5,11-methanodibenzo[*b,f*][1,5]diazocine (**TBAN3**) are still emissive. It is obvious that changing substitution positions has a marked influence on their luminescence properties.

1. Introduction

Organic emissive dyes have been extensively researched not only to explore their fundamental optical and electrical properties, but also to identify their potential applications in optoelectronic field. Numerous organic electroluminescent and photoluminescent (PL) compounds based on the fused polycyclic compounds such as naphthalene [1–3], anthracene [4–6], phenanthrene [7–9] and pyrene [10–12] have been studied. Among them, anthracene is an important organic luminary during the development of organic optoelectronics. For instance, the first organic electroluminescence was observed from its single crystals [13]. Owing to its strong fluorescence and high charge transporting properties, anthracene and its derivatives have been utilized as promising building blocks for functional materials with unique optical and optoelectronic properties, including conjugated small molecules, oligomers and polymers. Because of their high potential for blue light-emitting devices, the design and synthesis of new anthracene derivatives with improved color purity, luminescence efficiency and stability are still of strong interest [14–16].

It is well-known that the twisting conformation of the dyes can prevent detrimental exciton interactions in the solid state. Substantial rigidity in solution together with twisted conformations in the solid within a single molecule seems contradicted and virtually impossible. Fortunately, it is found that Tröger's base is an excellent natural candidate for luminescence material in both solid and solution [17–21] because of its twisted framework. First of all, Λ-shaped geometry configuration of Tröger's base is theoretically disadvantageous to form π-π close stacking and dipole-dipole interaction. Secondly, the highly rigidity and steric hindrance can restrict the internal rotation and reduce non-radioactive transition.

Herein, we report a new kind of organic dyes based on the anthracene moiety and Λ-shaped Tröger's Base, in which the carbon-carbon triple bond was used to bridge these two groups to ensure the rigidity of the whole molecular and the planarity of both side. In addition, positional isomers have attracted much attention in the optoelectronic field since their optical properties can be tuned by changing the position of substituents [22–25]. Hence, great number of previous research on isomers with optical properties concentrated on the positions of the skeletons. In this paper, we turned our eyes on the positions of the substituents. Based on these perceptions, we designed and synthesized three isomers (**TBAN1**, **TBAN2** and **TBAN3** as shown in Scheme 1) and investigated the effect of substitution position of anthracene units on the photophysical properties.

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https://doi.org/10.1016/j.tet.2018.07.039
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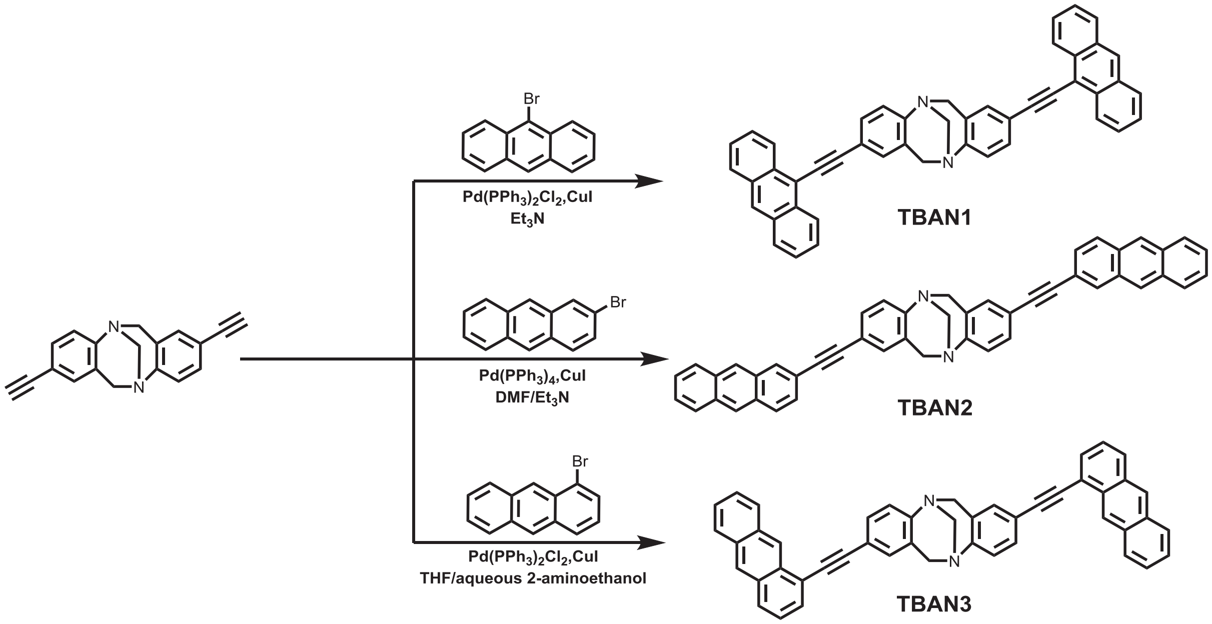

Scheme 1. Synthetic routes of **TBAN1**, **TBAN2** and **TBAN3**.

2. Result and discussion

2.1. Design and synthesis

We designed three new isomers based on Tröger's base and devised a similar route for their synthesis. All of them were synthesized via Sonogashira coupling reaction with different conditions. **TBAN1** can be synthesized in moderate yield (30%) via common Sonogashira coupling reaction condition that Et_3N was used as solvent, CuI and $Pd(PPh_3)_2Cl_2$ were used as catalysts. However, only trace amount of target product was obtained for **TBAN2** and no reaction took place for compound **TBAN3** under the same reaction condition. For **TBAN2**, when DMF is employed in the reaction system, the desired product can be obtained in a relatively high yield (35%) [26]. In the case of **TBAN3,** 2-aminoethanol is the key factor to make the Sonogashira coupling reaction occur [27]. Consider the main difference of these three compounds is the substituted positions of anthracene which may cause the reactivity and solubility of the target compounds. For anthracene, position 9 is the most reactive site in the molecule [28]. In addition, **TBAN1** has the best solubility among the three compounds. So **TBAN1** is easily to be synthesized by common Sonogashira coupling reaction conditions. In the case of **TBAN2** who has the poorest solubility, it could be synthesized when DMF was employed as solvent in the reaction system. However, **TBAN3** cannot be synthesized by the two conditions mentioned above until 2-aminoethanol who is an effective base [29] was used as the base. We suppose that 2-aminoethanol is more reactive than Et_3N, so it can effectively promote reaction when come to the less reactive 1 position of anthracene. Therefore, we think the major differences in the synthesis of these three isomers are mainly caused by the divided reactivity owing to the different substituted positions of anthracene.

All the target compounds were characterized by NMR spectroscopy and mass spectrometry to confirm their molecular structures.

2.2. Photophysical properties

Absorption and fluorescence spectra of compounds **TBAN1**, **TBAN2** and **TBAN3** were recorded in various solvents with different polarity using 1.0×10^{-5} mol/L solutions. The absorption peak wavelength, fluorescence peak wavelength and fluorescence quantum yields were summarized in Table 1. As shown in Fig. 1 and Table 1, **TBAN1** exhibited two obvious absorption peaks at about 405 nm and 427 nm in organic solvents, and the λ_{max} was slightly affected by solvent polarity, probably because the dipole moments of the molecules in their ground state and excited state were almost the same [30]. However, an apparent emission band red shift was observed with increasing solvent polarity and the half-width increased gradually. The photoluminescence emission band shifted from ~430 nm in hexane (lowest polarity) to ~470 nm in DMSO (highest polarity), which corresponds to bathochromic shift of ~40 nm. Therefore, the emission properties of these molecules are highly depended on the solvent polarity, which can be attributed to the incorporation of the electron-donating aromatic group to the electron-withdrawing carbon-carbon triple bond and anthracene units. These results indicate that when excited by light, the dipole moment of the excited state is larger than the ground state, which suggests that increasing the polarity of the solvent is beneficial for stabilizing molecules in the excited state. The absolute fluorescence quantum yields of **TBAN1** varied from 0.46 to 0.69 and the highest absolute fluorescence quantum yields were observed in benzene and toluene possibly owing to the similarity between molecules and these two solvents.

Absorption and fluorescence spectra of **TBAN2** in different solvents were depicted in Fig. S2 (See Supporting information) and its photophysical properties were shown in Table 1. The absorption spectra of **TBAN2** in all the studied solvents were found to be grossly similar which containing two bands, one around 325 nm and another around 356–397 nm. **TBAN2** showed negligible solvatochromism in absorption spectra, but pronounced red shifts were observed in the emission spectra from nonpolar solvent (hexane) to polar solvent (DMSO) which resulted in the increase of