



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

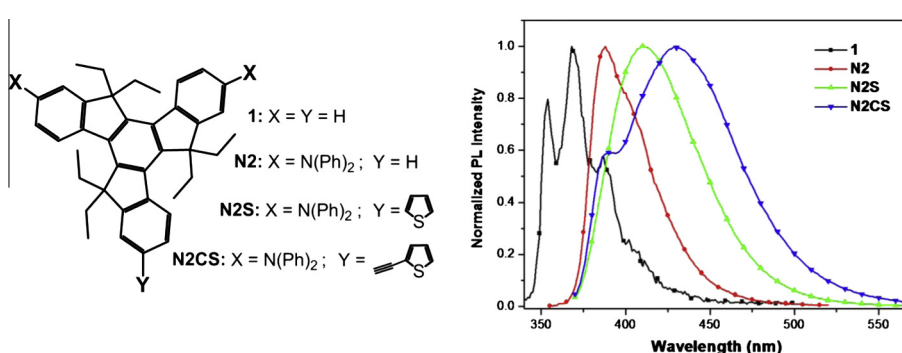
Asymmetric multibranching conjugated molecules: Synthesis, structure and photophysical properties

Li Zhao^{a,b}, Wenji Wang^a, Mao-Sen Yuan^{a,c,*}^a College of Science, Northwest A&F University, Yangling 712100, PR China^b Hospital, Northwest A&F University, Yangling 712100, PR China^c State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, PR China

HIGHLIGHTS

- Two truxene-cored asymmetric multibranching π -conjugated molecules were synthesized.
- The two compounds exhibit almost same absorption maxima, but different emission.
- The theoretical results reveal the HOMO \rightarrow LUMO transition is not their main transition.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 29 April 2014

Received in revised form 16 June 2014

Accepted 29 June 2014

Available online 8 July 2014

Keywords:

Photophysical properties

Crystal structure

Charge transfer

Truxene

Thiophene

ABSTRACT

The symmetric multibranching π -conjugated compounds with C₃ or C₆ configuration have been intensively studied. The reports on asymmetric multibranching compounds are very limited. In this work, we designed and synthesized two asymmetric multibranching π -conjugated molecules using truxene as the central core, diphenylamino and thiophenyl (or thiophenylethynyl) groups as the different branches respectively: 2,7-di(*N,N*-diphenylamino)-12-(2-thiophenyl)-5,5',10,10',15,15'-hexaethyltruxene and 2,7-di(*N,N*-diphenylamino)-12-(2-thiophenylethynyl)-5,5',10,10',15,15'-hexaethyltruxene. Their photophysical properties have been explored combining with their theoretical calculation and X-ray single-crystal structure of a key intermediate. Though their different π -conjugation length of branches, the two title compounds exhibit almost same absorption maxima. However, their emission peaks behave a gradual red-shift with the increase of the conjugation length. The theoretical calculation results indicate that the two asymmetric compounds behave a main transition from the HOMO – 1 to the LUMO or from the HOMO to the LUMO + 1 upon excited.

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Introduction

Multibranching organic π -conjugated molecules, due to their fascinating molecular architecture and unique properties, have

attracted great interest in this decade [1–7]. In comparison to the linear molecules and polymers, branching π -conjugated molecules have some advantages for applications in optoelectronic devices, for example, the three-dimensional architectures, well-defined molecular structure and good film-forming processing. In recent years, a large number of multibranching π -conjugated molecules have been exploited extensively in a wide range of applications as optoelectronic materials [8–14]. However, more research

* Corresponding author at: College of Science, Northwest A&F University, Yangling 712100, PR China. Tel./fax: +86 29 87092226.

E-mail address: yuanms@nwsuaf.edu.cn (M.-S. Yuan).

mainly focused on the symmetric molecular system. In other words, most of these multibranch molecules exhibit C_n symmetric configurations (mostly C_3 and C_6), and every branch of the same molecule behaves the same chemical structure. Studies that focus on the properties and structure–function relationship investigation of asymmetric multibranch molecules are very limited [15,16], which may be on account of the difficulty in synthesis.

Generally, multibranch optoelectronic molecules are constructed from an interior functional core with several photo- and electro-active branching units. Truxene (10,15-dihydro-5H-diindeno[1,2-a;1',2'-c]fluorene), due to its C_3 -symmetric skeleton and planar π -conjugated polyarene structure, has been intensively studied as a π -conjugated central core to fabricate branched optoelectronic molecules [17–29]. Herein, we are of particular interest to develop the asymmetric multibranch compounds using truxene as central unit. In order to endow the designed molecules with good optoelectronic properties as well as thermal and chemical stability, we availably functionalized truxene at its 2,7,12-positions with diphenylamino, thiophenyl and thiophenylethynyl respectively to get two asymmetric π -conjugated molecules: 2,7-di(*N,N*-diphenylamino)-12-(2-thiophenyl)-5,5',10,10',15,15'-hexaethyltruxene (**N2S**) and 2,7-di(*N,N*-diphenylamino)-12-(2-thiophenylethynyl)-5,5',10,10',15,15'-hexaethyltruxene (**N2CS**). In this work, we present a photophysical and theoretical calculation studies combining with the X-ray single-crystal structure of an intermediate.

Experimental section

Synthesis and characterizations of the subject compounds

Solvents for reactions and spectral measurements were dried and distilled before use. The reagents used for reactions were purchased from J&K Scientific Ltd. ^1H NMR spectra were recorded at 25 °C on Bruker Avance 500 MHz spectrometer using CDCl_3 as solvent. ^{13}C NMR spectra were recorded at 25 °C on Bruker Avance 125 MHz spectrometer using CDCl_3 as solvent. Element analyses (C, H, S) were performed using a PE 2400 autoanalyser. Mass spectrometry analyses were performed by a Bruker Biflex III matrix

assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometer.

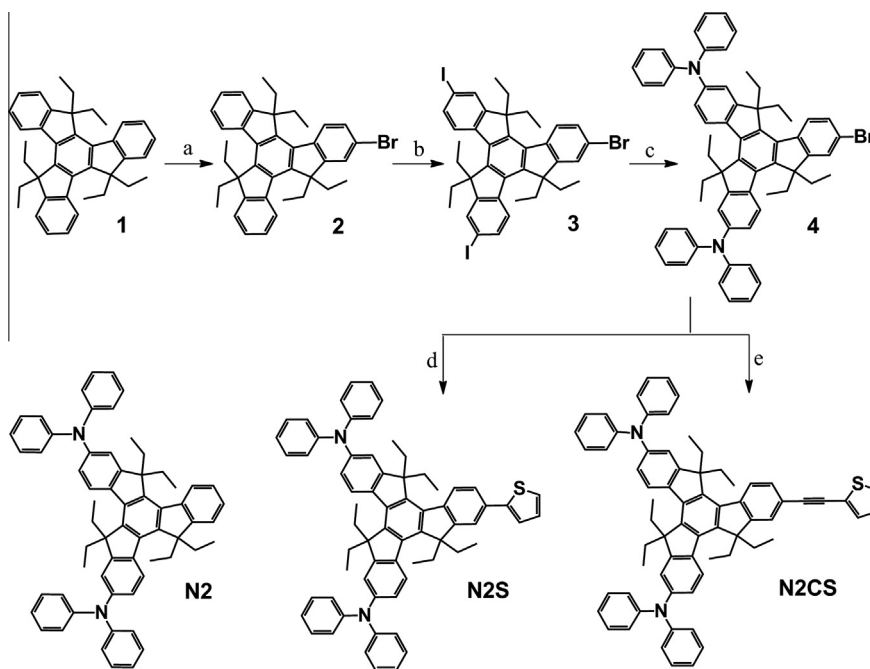
Compounds **1–4** and **N2** were synthesized according to literature methods reported by us [16].

Synthesis of compound N2S

A mixture of compound **4** (0.50 g, 0.54 mmol), 2-thiopheneboronic acid (0.10 g, 0.78 mmol), $\text{Pd}(\text{PPh}_3)_4$ (20 mg, 0.02 mmol), toluene (30 mL), ethanol (8 mL) and 2 M aqueous K_2CO_3 solution (2 mL) was heated and stirred at 80 °C under a nitrogen atmosphere for 24 h. The mixture were cooled to room temperature and poured into water (100 mL). After extraction with dichloromethane (DCM), the organic phase was dried over Na_2SO_4 . The solvent was removed and the residue was purified by column chromatography on silica gel using DCM-hexane (1:20) as the eluent to get compound **N2S** (0.16 g, 31.9%). **N2S**: a yellow powder, m.p. 156–158 °C. ^1H NMR (CDCl_3 , 500 MHz, ppm): δ 0.21–0.28 (m, 18H), 1.89–2.15 (m, 6H), 2.84–2.99 (m, 6H), 7.02–7.12 (m, 6H), 7.32–7.33 (m, 3H), 7.46–7.49 (m, 2H), 7.55–7.58 (m, 16H), 7.57–7.67 (m, 2H), 8.09–8.27 (m, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 154.22, 153.67, 152.67, 147.96, 129.24, 129.05, 128.24, 128.09, 126.35, 126.04, 125.31, 124.92, 124.59, 124.21, 122.95, 122.88, 122.69, 122.27, 121.98, 119.47, 117.66, 67.98, 56.65, 29.40, 29.19, 25.63, 21.46, 8.69, 8.65, 8.61. MALDI-TOF: m/z 927.3 [M^+], 898.9 [$\text{M}-29$] $^+$. Elemental Anal. Calcd. for $\text{C}_{67}\text{H}_{62}\text{N}_2\text{S}$: C, 86.78; H, 6.74; N, 3.02; S, 3.46. Found: C, 86.71; H, 6.84; S, 3.35.

Synthesis of compound N2CS

A mixture of compound **4** (0.50 g, 0.54 mmol), 2-ethynylthiophene (0.10 g, 0.84 mmol), $\text{Pd}(\text{PPh}_3)_4$ (20 mg, 0.02 mmol), $n\text{-Bu}_4\text{NF}$ (50 mg), THF (20 mL) and triethylamine (10 mL) was heated to reflux with stirring after flushed with nitrogen for half an hour. After reacting for 10 h under nitrogen, the mixture were cooled to room temperature and poured into water (100 mL). After extraction with CHCl_3 several times, the organic phase was dried over MgSO_4 . The solvent was removed and the residue was purified by column chromatography on silica gel using DCM-hexane (1:10) as eluent to get compound **N2CS** (0.32 g, 62%). **N2CS**: a



Scheme 1. Synthesis of title compounds **N2S** and **N2CS**. For comparison, compound **N2**, a known compound reported in our previous study, is also shown. (a) Propylene carbonate, NBS, 60 °C, 2 h; (b) HIO_3 , I_2 , $\text{CH}_3\text{COOH}-\text{H}_2\text{SO}_4-\text{H}_2\text{O}-\text{CCl}_4$, 80 °C, 4 h; (c) Diphenylamine, K_2CO_3 , Cu (powder), 18-crown-6-ether, 1,2-dichlorobenzene, reflux, 8 h; (d) 2-Thiopheneboronic acid, $\text{Pd}(\text{PPh}_3)_4$, K_2CO_3 , Toluene/ethanol/ H_2O , under N_2 , 80 °C, 24 h; (e) 2-ethynylthiophene, $\text{Pd}(\text{PPh}_3)_4$, $n\text{-Bu}_4\text{NF}$, Et_3N , THF, under N_2 , reflux, 10 h.

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