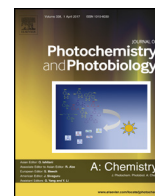




Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

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



Invited paper

Excimer formation from partially overlapped anthracene dimer based on saddle-shaped cyclooctatetrathiophene as spacer

Chunmei Zhao^{a,c}, Xing Cai^a, Zhiying Ma^a, Jianwu Shi^a, Li Xu^{b,*}, Hua Wang^{a,*}

^a Engineering Research Center for Nanomaterials, Henan University, Kaifeng, 475004, PR China

^b College of Chemistry and Chemical Engineering, Henan University, Kaifeng, 475004, PR China

^c Institute of Nanostructured Functional Materials, Huanghe Science and Technology College, Zhengzhou, 450006, PR China

ARTICLE INFO

Article history:

Received 27 June 2017

Received in revised form 12 August 2017

Accepted 13 August 2017

Available online xxx

ABSTRACT

With “saddle” shaped tetra[3,4-Thienylene] (TT) as a rigid 3D spacer, three anthryl substituted TT compounds, 1-(anthracen-9-yl)[3,3'-bithiophene] (TTA-1), 1,7-di(anthracen-9-yl)-[3,3'-bithiophene] (TTA-2) and 1,12-di(anthracen-9-yl)[3,3'-bithiophene] (TTA-3) were designed and synthesized. Their physical behaviors including NMR spectra, crystal structures and spectroscopic properties were studied. Due to the steric hindrance from TT moiety to avoid the dimer formation between molecules, TTA-1 and TTA-2 show monomer anthracene emission both in solution and rigid state, and a mixture of monomer and excimer emission in aggregation state. Bearing two ipsilateral anthracene moieties in molecule, TTA-3 gives a twisted and end-overlapped dimer in the ground state, and shows excimer emission only in solution, aggregation state and rigid state. In addition, a model compound, 2,2'-di(anthracen-9-yl)-5,5'-di(trimethylsilyl)-[3,3'-bithiophene] (BTA) was prepared, which shows monomer emission in both solution and rigid state, but gives excimer emission in the aggregation due to its extended conformation in solution and intermolecular dimer arrangement in its crystal and aggregation state.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

As one of acenes, anthracene has been widely investigated in both chemistry and material science for many years. Because of the excellent luminescence behaviors, anthracene derivatives have shown their utilization in organic functional materials, such as organic field effect transistors (OFETs), organic light-emitting diode (OLED), etc. [1–3]. The phenomenon of excimer emission for anthracene and its derivatives is of special interest in photochemistry, supermolecular chemistry, photobiology and polymer science [4–7].

The excimer formation for anthracene is from its excited dimer, which has four possible structures, normal dimer, twisted dimer, offset dimer and T-shaped dimer (Fig. 1) [8–10]. Normal dimer has a well-overlapped “sandwich” structure, in which two anthracene units show a “face to face” assembly. The offset and twisted dimers (Fig. 1) also show excimer emission [8]. More interesting, Yang et al. presented an “end to face” structural T-shaped excimer between two anthracene moieties from a highly luminescent bis

(9-anthryldiamine) zinc(II) complex [10], which showed strong excimer emission both in solution and in solid state.

With increase of concentration of anthracene moiety, the intermolecular dimerization can be formed gradually. However, the formation of intramolecular excimer does not depend on the concentration of substrate, but depend on the suitable spacer (or linkage) between two anthracene moieties. On the one hand, the chain-shaped spacers, such as trimethylene [11], 1,1,3,3-tetramethyldisiloxane [12], ether chain [13,14], etc. have been investigated during past years. Such one dimensional spacers should be flexible enough for the construction of anthracene dimer in the ground state or excited state. On the other hand, the three-dimensional (3D) spacer is seldom employed for such issue due to the challenge of organic synthesis. Bouas-Laurent et al. reported that bis (anthraceno)-crown ether shows increased intramolecular excimer emission and effective photochemical isomerization by the presence of complexed metal ions. The involved coordination makes two anthracene moieties in well-overlapped conformation in space to make a dimer in the ground state [15]. Prasad et al. reported aggregation-controlled anthracene excimer emission with polyamidoamine dendrimers as spacer [16]. Such 3D spacer (e.g. dendrimer) may be extended by H-bonding or π - π interaction to form a suitable conformation of excimer.

* Corresponding authors.

E-mail address: hwang@henu.edu.cn (H. Wang).

<http://dx.doi.org/10.1016/j.jphotochem.2017.08.030>

1010-6030/© 2017 Elsevier B.V. All rights reserved.

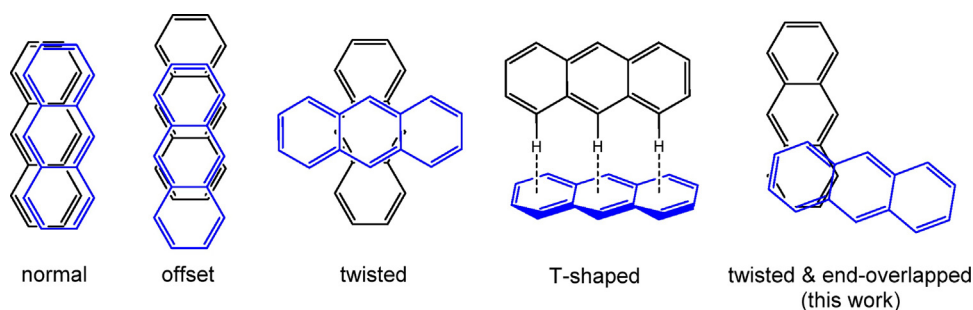


Fig. 1. The possible structures of excimers for anthracene dimers[8].

However, 3D spacer with rigid framework should be novel one employed for formation of anthracene excimer. Cyclooctatetrathiophene (**COTh**) is such kind of rigid 3D spacer with “saddle” shaped molecular skeleton known since 1974 [17,18]. **COTh** has shown its application in molecular muscles [19] and electromechanical actuators [20,21] reported by Marsella during past 40 years. According to our best knowledge, **COTh** has not been used as spacer for the investigation of photochemistry. **COTh** has several isomers [22], and tetra[3,4-Thienylene] (**TT**) [18] is one of the first two isomers reported by Kauffmann [17,18]. Possessing an inherently nonplanar saddle-shaped geometry with D_{2d} symmetry, **TT** can be taken as a special 3D spacer for bearing aromatic groups, such as anthracene moieties. Extended from the rigid molecular skeleton of **TT**, two anthracene moieties can be fixed in both distance and dihedral angle. Therefore, study on the excimer formation for anthracene with **TT** as 3D spacer should be of high interest.

In this work, we design and synthesize three anthryl substituted **TT** compounds, 1-(anthracen-9-yl)[3,3'-bithiophene] (**TTA-1**), 1,7-di(anthracen-9-yl)[3,3'-bithiophene] (**TTA-2**) and 1,12-di(anthracen-9-yl)[3,3'-bithiophene] (**TTA-3**) (Fig. 2). **TTA-2** and **TTA-3** are isomers bearing two anthracene moieties in different ways of connection to the framework of **TT**. We studied on their physical behaviors including NMR spectra, crystal structures and spectroscopic properties, and found a novel excimer emission from **TTA-3**, which has two ipsilateral anthracene moieties forming a twisted and end-overlapped dimer in the ground state. **TTA-3** shows strong excimer emission in solution, aggregation state and rigid state. For further understanding the rich photophysical behaviors of **TTA-1** to **TTA-3**, 2,2'-di(anthracen-9-yl)-5,5'-di(trimethylsilyl)-[3,3'-bithiophene] (**BTA**) was prepared as a model compound, and its spectroscopic properties were explored at same time.

2. Experimental sections

2.1. Materials and apparatus

Ether and tetrahydrofuran (THF) for use were freshly distilled from sodium/benzophenone prior to use. Concentration of *n*-BuLi

(hexane) was determined by titration with *N*-pivaloyl-*o*-toluidine [23]. Column chromatography was carried out on silica gel (300–400 or 200–300 mesh). Analytical thin-layer chromatography was performed on glass plates of Silica Gel GF-254 with detection by UV. Standard techniques for synthesis under inert atmosphere, using gasbag and Schlenk glassware equipped with an 8-mm PTFE vacuum stop-cock were employed. All starting materials and reagents were commercially available.

NMR spectra were obtained using $CDCl_3$ and $DMSO-d_5$ as solvents. The chemical shift references were as follows: (1H) $CDCl_3$, 7.26 ppm ($CDCl_3$); (^{13}C) $CDCl_3$, 77.00 ppm ($CDCl_3$); (1H) $DMSO-d_6$, 2.50 ppm ($DMSO-d_5$); (^{13}C) $DMSO-d_6$, 39.52 ppm ($DMSO-d_6$). IR spectra were obtained using an FT-IR instrument, equipped with an ATR sampling accessory. HRMS spectra were carried out at TOF MS (EI^+) or FTMS (ESI). Melting point determination was taken on a Melt-Temp apparatus and was uncorrected. UV–vis spectra were obtained with a single-beam spectrophotometer at room temperature. PL spectra were recorded on HORIBA JY FluoroLog-3 equipped with quartz cuvettes of 1 cm path length at room temperature. Solvents for UV–vis and emission spectroscopic measurements were spectrographically pure as received.

The X-ray crystallographic analyses were performed using crystals of compounds **TTA-2**, **TTA-3** and **BTA** with size $0.04 \times 0.03 \times 0.02$, $0.20 \times 0.16 \times 0.08$ and $0.20 \times 0.10 \times 0.06$ mm, respectively. The intensity data were collected with ω scan mode on a diffractometer with CCD detector using $Cu K\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$) or $Mo K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. The data were corrected for Lorentz and polarisation effects and absorption corrections were performed using SADABS program [24]. Using Olex2, the structures were solved with the XT structure solution program using intrinsic phasing and refined with the XL refinement package using least squares minimization [25–27]. It should be noted that for **TTA-3** crystal, the chloroform molecules were highly disordered and could not be refined satisfactorily, thus the SQUEEZE routine of PLATON was used to remove the contributions to the scattering from the solvent molecules [28,29]. The positions of hydrogen atoms were calculated theoretically and included in the final cycles of refinement in a riding model along with attached carbons. Further details are in the deposited CIFs. Slow evaporation of solutions of

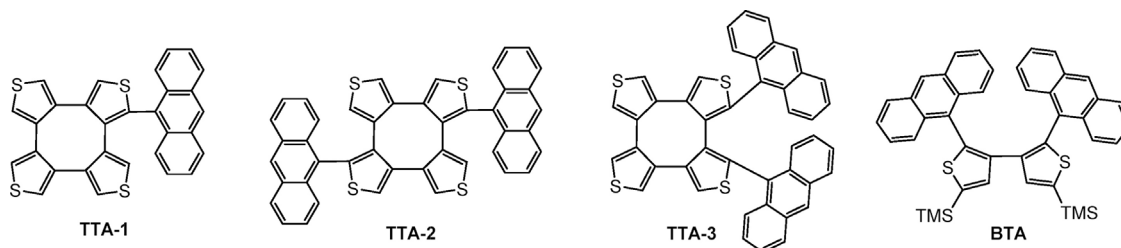


Fig. 2. The molecular structures of three anthracene substituted cyclooctatetrathiophenes (**TTA-1**, **TTA-2** and **TTA-3**) and model compound **BTA**.

Download English Version:

<https://daneshyari.com/en/article/6492755>

Download Persian Version:

<https://daneshyari.com/article/6492755>

[Daneshyari.com](https://daneshyari.com)