Chemistry
A European Journal

Chemistry
Europe
European Chemical
Societies Publishing

Title: Anthrathiadiazole Derivatives: Synthesis, Physical Properties and Two-photon Absorption

Authors: Qichun Zhang, Mingxuan Fan, Guangsheng Chen, Yu Xiang, Junbo Li, Xianglin Yu, Wenying Zhang, Xueting Long, Liang Xu, Jinjun Wu, and Ze Xu

To be cited as: *Chem. Eur. J.* 10.1002/chem.202100307

Link to VoR: https://doi.org/10.1002/chem.202100307

WILEY-VCH

10.1002/chem.202100307

Anthrathiadiazole Derivatives: Synthesis, Physical Properties and Two-photon Absorption

Mingxuan Fan [a], Guangsheng Chen [a], Yu Xiang [a], Junbo Li *[a], Xianglin Yu [c], Wenying Zhang [b], Xueting Long [b], Liang Xu *[b], Jinjun Wu [a], Ze Xu [c], Qichun Zhang *[d]

[a] Mr, M. Fan, Mr. G. Chen, Mr Y. Xiang, Prof. J. Li, Mr. J. Wu
School of Chemistry and Environmental Engineering, Key Laboratory for Green Chemical Process of Ministry of Education
Wuhan Institute of Technology
Wuhan, China
E-mail: jbliwit@163.com

[b] Ms W. Zhang, Ms X. Long, Dr. L. Xu
Department of Chemistry and Key Laboratory for Preparation and Application of Ordered Structural Materials of Guangdong Province
Shantou University
Shantou, China
E-mail: xuliang@stu.edu.cn

[c] Prof. X. Yu, Mr. Z. Xu
School of Chemical Engineering and Pharmacy
Wuhan Institute of Technology
Wuhan, China

[d] Prof. Q. Zhang
Department of Materials Science and Engineering
City University of Hongkong
E-mail: qiczhang@cityu.edu.hk

Supporting information for this article is given via a link at the end of the document.

Abstract: Anthrathiadiazole is a key synthon for the construction of large azaacenes, however, the attachment of different substituents onto the skeleton of anthrathiadiazole is difficult but highly desirable because it could be easy to enrich the structures of azaacenes. Here, we demonstrate that anthrathiadiazole derivatives with -Br, -CN, and -OCH_3 groups could be easily constructed through a simple [4+2] cycloaddition reaction between a, a, a’, a’-tetrabromo o-xylenes derivatives and benzo[c][1,2,5]thiadiazole-4,7-dione. The structures of the as-prepared compounds with different substituents were carefully characterized. Moreover, the basic physical properties of the as-prepared anthrathiadiazole derivatives were fully investigated, where the cyano-substituted derivative **(BTH-CN)** has the highest stability and the methoxy-substituted derivative (**BTH-OCH_3)** is easy to be oxidized. Moreover, the two-photon absorption (TPA) characteristics of different anthrathiadiazoles are also studied by using the femtosecond Z-scan technique. The results show that the fused anthrathiadiazole skeletons possess large TPA cross-section values δ_2 in the range of 3000-5000 GM, where the nature, position and strength of the substituted groups have strong effect on these values.

Introduction

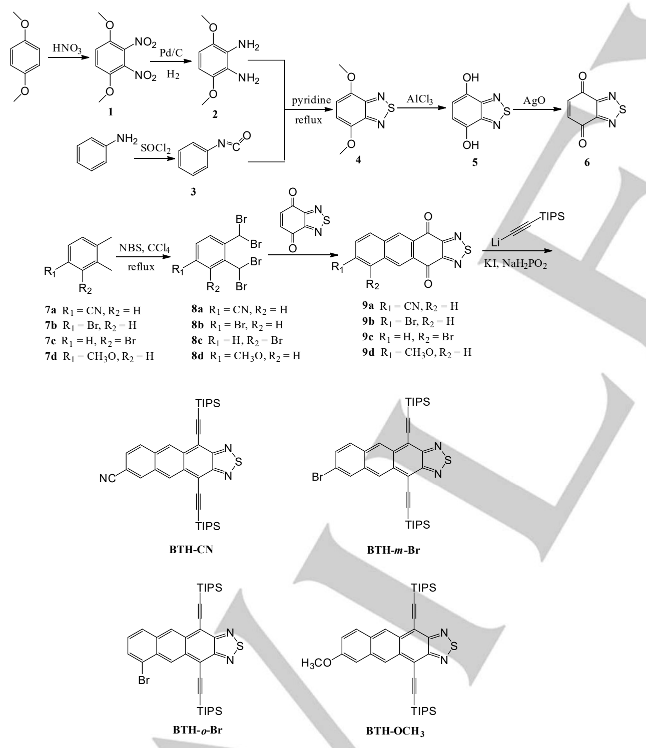
Acenes, consisting of linearly-fused benzene rings, have been widely investigated as active elements in organic electronics[1] such as organic light-emitting diodes (OLED)[2], organic field-effect transistors (OFET)[3], organic photovoltaics (OPVs)[4], etc. However, their synthesis, especially for pentacene and higher acenes (n>5), is very difficult and tedious since the increasing number of the fused benzene rings leads to a dramatic decrease in their stability[5]. Thus, many methods have been developed to address this issue, where the most promising one is the replacement of sp^2 C with hetero-atoms (*i.e.* N, P, O) in the skeletons of acenes[6]. Specifically, N-heterocycle-containing acenes (azaacenes) have been widely investigated because of their adjustable charge-transporting properties and excellent stability, which would have great potential applications in organic optoelectrical devices[7]. More recently, azaacenes have also been demonstrated to display two-photon absorption (TPA)[8]. Such property would endow them new applications in various fields including photodynamic therapy[9], data storage[10], optical switching[11] and energy up-conversion[12]. Thus, preparing new synthons to construct this type of N-heteroacenes is highly desirable.

As one type of key synthons developed to approach diverse azaacenes, anthrathiadiazole and their derivatives[13], have been demonstrated to show promising charge transport behaviors in organic electronics[14]. More importantly, anthrathiadiazole derivatives can also be converted into stable diamine intermediates through the reduction of lithium aluminum hydride (LAH), which can be employed as powerful “building blocks” to construct diverse azaacenes[15]. These azaacenes might be good TPA candidates.

The traditional methods for the synthesis of anthrathiadiazole are to use 2,3-dibromoanthracene-1,4-dione as the starting materials, which firstly reacts with potassium phthalimide through a nucleophilic substitution reaction, followed by the hydrolysis with hydrazine to afford the intermediate diaminoquinone. Then, this intermediate could react with thionyl chloride in the refluxing condition to form the thiadiazole ring, which could further react with different alkynyl lithium reagents to produce anthrathiadiazole[13a]. One should note that the report on the synthesis of the substituted anthrathiadiazoles is rare. However, the substituted anthrathiadiazoles are very important because they are not only key building units to enrich the structures of anthrathiadiazole-based materials but also endow us the strong power to modulate their optical and electronic properties. Such gap dramatically encourages us to attach different substituted groups on the frameworks of anthrathiadiazole and investigate their corresponding properties.

Herein, we use potassium iodide as a nucleophile to eliminate the Br group on the *a, a, a', a'*-tetrabromo-o-xylenes derivative, followed by the [4+2] cycloaddition reaction with benzo[c][1,2,5]thiadiazole-4,7-dione to produce four novel derivatives (**BTH-*m*-Br**, **BTH-*o*-Br**, **BTH-CN** and **BTH-OCH₃**)[16]. Besides the effects of substituents on their normal optoelectronic properties, the TPA property of the as-prepared anthrathiadiazole-based materials are also studied. We find that the nature, position and strength of the substituted groups on the framework have strong effect on TPA δ_2 values.

Compounds **1-6** and **8a-c** are prepared according to the reported procedure[17]. In order to obtain anthrathiadiazole derivatives with different substitutes, a simple [4+2] cycloaddition reaction with potassium iodide as the nucleophilic reagent is used to construct four anthrathiadiazole derivatives between *a, a, a', a'*-tetrabromo o-xylenes derivatives and benzo[c][1,2,5]thiadiazole-4,7-dione. Note that Br atom can also act as the active site for the extension of π conjugate system, which might provide a new strategy for the enrichment of heteroacenes.



Scheme 1. Synthetic routes to the four anthrathiadiazole derivatives.

The UV–vis spectra of four compounds (**BTH-CN, BTH-*m*-Br**, **BTH-*o*-Br**, **BTH-OCH₃**) are recorded in CH_2Cl_2. All materials show two sets of absorption peaks between 350-450 nm and 500-750 nm, where the maximum absorption peaks for **BTH-CN, BTH-*m*-Br**, **BTH-*o*-Br**, and **BTH-OCH₃** are located at 647 nm, 650 nm, 651 nm and 668 nm with shoulder peaks at 597 nm, 602 nm, 605 nm and 627 nm, respectively, which are attributed to the intramolecular charge transfer (ICT). The maximum absorption peaks of **BTH-CN**, **BTH-*m*-B**r, and **BTH-*o*-Br** are similar to that of the reported parent compound **BTH-C** (λ_{max} = 656 nm)[18]. However, the maximum absorption peak of **BTH-OCH₃** red-shifts nearly 12 nm, which may be caused by the stronger ICT due to the electron-donating group ($-OCH_3$). As shown in Figure 1b, all compounds (**BTH-CN**, **BTH-*m*-Br**, **BTH-*o*-Br**, **BTH-OCH₃**) display different emission peaks at 684 nm, 700 nm, 701 nm and 739 nm, respectively. Compared with **BTH-*m*-Br**, the emission wavelength of **BTH-CN** is blue-shifted by 16 nm, while **BTH-OCH₃** is red-shifted by 39 nm, associating with an obviously quenching fluorescence. Since there is a strong ICT process in **BTH-OCH₃**, when the electrons in **BTH-OCH₃** are excited by light, the intersystem crossing happened, which induces the quenching of the fluorescence. The fluorescence quantum yields (Φ) of **BTH-CN, BTH-*m*-Br**, **BTH-*o*-Br**, and **BTH-OCH₃** in CH_2Cl_2 are measured to be 0.044, 0.029, 0.022 and 0.005, respectively, with 9,10-diphenylanthracene as the standard sample (Φ = 0.95 in CH_2Cl_2)[19].

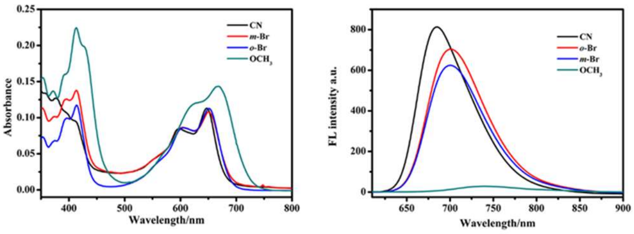


Figure 1. UV-vis absorption (a) and Fluorescence spectra (b) of **BTH-CN**, **BTH-*m*-Br**, **BTH-*o*-Br**, and **BTH-OCH₃** (10^{-5} M in CH_2Cl_2).

The electrochemical properties of **BTH-CN**, **BTH-*m*-Br**, **BTH-*o*-Br**, and **BTH-OCH₃** are measured by the cyclic voltametric (CV) analysis in CH_2Cl_2 solution with 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as the supporting electrolyte. Ferrocene is used as an internal standard. As shown in Figure 2, the CV curves of **BTH-*m*-Br** and **BTH-*o*-Br** are very similar to each other, displaying two reversible reduction waves and one reversible oxidation wave. However, **BTH-OCH₃** shows one reversible reduction wave, one reversible oxidation wave and one irreversible oxidation wave, while **BTH-CN** exhibits two reversible reduction waves and one reversible oxidation wave. The onset oxidative potentials of **BTH-CN**, **BTH-*m*-Br**, **BTH-*o*-Br**, and **BTH-OCH₃** are measured to be 0.87 V, 0.72 V, 0.70 V, 0.50 V, respectively, indicating that **BTH-CN** is the most difficult one to be oxidized among all compounds due to the existence of the stronger withdrawing group -CN. The HOMO energy levels of **BTH-CN**, **BTH-*m*-Br**, **BTH-*o*-Br** and **BTH-OCH₃** are calculated to be -5.67 eV, -5.52 eV, -5.50 eV, and -5.30 eV, respectively, through the equation of $E_{HOMO} = -(E_{onset}^{ox} + 4.80)$ eV.

Table 1. Optical and electrochemical data of **BTH-CN**, **BTH-*m*-Br**, **BTH-*o*-Br** and **BTH-OCH₃**.

Comp	E_{onset}^{ox} (V)^a	E_{onset}^{red} (V)^a	LUMO (eV)^b	HOMO (eV)^c	E_{gap} (eV)^d	E_{gap}/λ_{onset} (eV / nm)^e	HOMO (eV)^f	LUMO (eV)^f	E_{gap} (eV)^f
CN	0.87	-0.91	-3.89	-5.67	1.78	1.81/684	-5.37	-3.5	1.87
***m*-Br**	0.72	-1.03	-3.77	-5.52	1.75	1.77/700	-5.15	-3.28	1.87
***o*-Br**	0.70	-1.06	-3.74	-5.50	1.76	1.77/701	-5.17	-3.28	1.89
OCH_3	0.50	-1.19	-3.61	-5.30	1.69	1.68/739	-4.93	-3.07	1.86

(a) The as-obtained values from cyclic voltammograms in CH_2Cl_2; (b) $E_{LUMO} = -(4.8 + E_{onset}^{red})$; (c) $E_{HOMO} = -(4.8 + E_{onset}^{Ox})$; (d) $E_{gap} = E_{LUMO} - E_{HOMO}$; (e) Optical band gap, $E_{gap} = 1240/\lambda_{onset}$; (f) The as-obtained values from theoretical calculations.

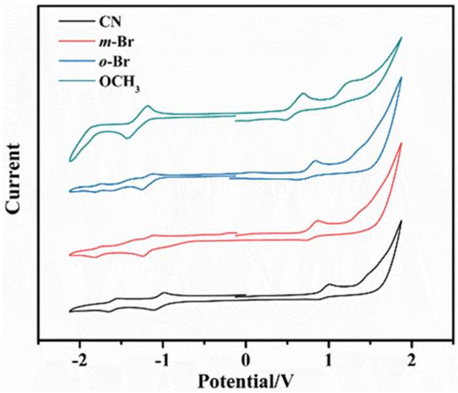


Figure 2. Cyclic voltammetry curves of **BTH-CN**, **BTH-m-Br**, **BTH-o-Br** and **BTH-OCH₃** in CH_2Cl_2 solution containing 0.1 M TBAP electrolyte. Scanning rate: 100 mV/s.

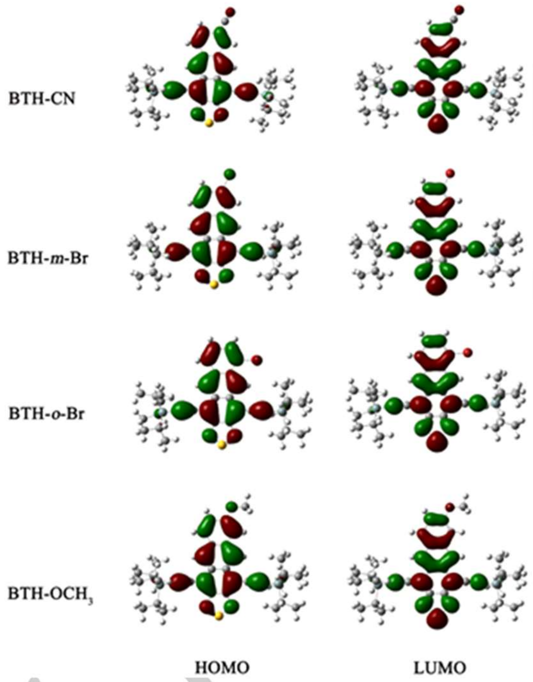


Figure 3. Wave functions for the HOMO and LUMO of **BTH-CN**, **BTH-m-Br**, **BTH-o-Br** and **BTH-OCH₃**.

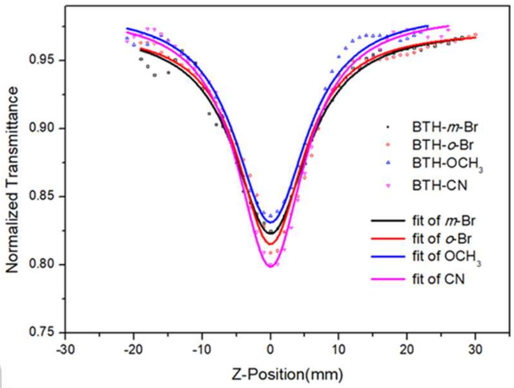


Figure 4. The open-aperture Z-scan results of **BTH-CN**, **BTH-m-Br**, **BTH-o-Br** and **BTH-OCH₃**.

The onset reductive potentials of **BTH-CN**, **BTH-*m*-Br**, **BTH-*o*-Br** and **BTH-OCH₃** are measured to be -0.91 V, -1.03 V, -1.06 V, -1.19 V, respectively, and the LUMO energy levels are calculated to be -3.89 eV, -3.77 eV, -3.74 eV, -3.61 eV respectively, through the equation of $E_{LUMO} =- (4.8 + E_{onset}^{red})$ eV[20] . The change trends in HOMO and LUMO energy levels and bandgaps of **BTH-CN**, **BTH-*m*-Br**, **BTH-*o*-Br** and **BTH-OCH₃** are consistent with the results from the theoretical calculations.

The molecular geometries of **BTH-CN**, **BTH-*m*-Br**, **BTH-*o*-Br** and **BTH-OCH₃** are optimized by using density functional theory (DFT) at the B3LYP/6-31G* level[21]. The ground state frontier molecular orbitals of the optimized molecules are also calculated. As shown in Figure 3, the HOMO orbitals of **BTH-CN**, **BTH-*m*-Br**, **BTH-*o*-Br** and **BTH-OCH₃** are similar to each other, and the LUMO orbitals of **BTH-CN**, **BTH-*m*-Br**, **BTH-*o*-Br** and **BTH-OCH₃** are also similar. All HOMOs are mainly delocalized on anthracene unit, thiadiazole ring except sulfur atom and alkyne groups, while all LUMOs are mainly localized on anthracene unit, thiadiazole ring including sulfur atom and alkyne groups, respectively. Note that the calculated HOMO energy levels are close to the results from CV experiment, which have been summarized in Table 1.

Actually, there are two main methods including two-photon excited fluorescence (TPEF) and Z-scan techniques for the measuring of TPA cross sections. The TPEF method is based on a TPA-induced fluorescence intensity measurement, where this method requires the fluorescent sample, limiting its application on some nonfluorescent systems. For the Z-scan method, the sample is moved along the path of a focused laser beam, and the light intensity as a function of its position along the z-axis is recorded. The limitation of this method is that other effects such as thermal lens effect may contribute to the 2PA cross-sections.[22] The two-photon absorption properties of **BTH-CN**, **BTH-*m*-Br**, **BTH-*o*-Br** and **BTH-OCH$_3$** are characterized by an open-aperture femtosecond Z-scan technique. The excitation source is a Ti:sapphire oscillator seeded regenerative amplifier (pulse energy of 1.3 mJ at 800 nm) with an adjustable excitation intensity. The as-obtained Z-scan curves (Figure 4) indicate that **BTH-CN**, **BTH-*m*-Br**, **BTH-*o*-Br** and **BTH-OCH$_3$** have TPA properties with the cross-section values (δ_2) of 3167 GM, 3461 GM, 3179 GM and 4913 GM, respectively. Our results clearly indicate that the value of the TPA cross sections (δ_2) strongly depends on the nature, position, and strength of the substituted groups on the same frameworks. Since Br atom is a weaker electron-withdrawing group than cyano species, the TPA cross sections (δ_2) of **BTH-*m*-Br** (3461) and **BTH-*o*-Br** （3179） are larger than that of **BTH-CN (**3167). Comparing to the Br position, the δ_2 of *m*-substituted **BTH** is much larger than the o-substituted one. As to the electron-donating group methoxyl, the two-photon absorption cross section value is the strongest one. Our results clearly confirm that the electron-rich group on the electron-deficient frameworks normally produces the larger TPA cross-sections δ_2. Moreover, some recently reported acene and nanographene-based TPA materials were listed in table S1.

Table 2. The TPA cross-sections δ_2 at 800 nm for **BTH-CN**, **BTH-m-Br**, **BTH-o-Br** and **BTH-OCH$_3$** measured by an open-aperture Z-Scan technique.

Comp	δ_2^{max}/GM
BTH-*m*-Br	3461
BTH-*o*-Br	3179
BTH-OCH$_3$	4913
BTH-CN	3167

Conclusion

In conclusion, we have prepared four anthrathiadiazole derivatives with different substituents by a simple [4+2] cycloaddition reaction between thiadiazolequinones and a, a, a', a'-tetrabromo o-xylene derivatives. The photophysical, electrochemical and two-photon absorption (TPA) properties of the as-prepared compounds were investigated. The as-prepared compounds not only exhibited a potential nonlinear optical application, but also could have a great potential to enrich the number of azaacenes. We also found that the TPA cross-sections δ_2 is strongly affected by the nature, position, and strength of the substituted groups on the same electron-deficient frameworks. Generally, electron-donating and weaker electron-accepting groups give larger δ_2 value.

Acknowledgements

This work was supported by National Science Foundation of China (No. 51203127, 20901063, 52073167 and 21702132), Guangdong Basic and Applied Basic Research Foundation. National Training Program of Innovation and Entrepreneurship for Undergraduates (201810490019). QZ thanks the support from starting funds from City University of Hongkong.

Keywords: azaacene • anthrathiadiazole • synthon • two-photon absorption • cycloaddition

(1) For recent reviews: a) Q. Ye, C. Y. Chi, *Chem. Mater.* **2014**, *26*, 4046-4056; b) J. B. Li, S. Chen, Z. L. Wang, Q. C. Zhang, *Chem. Rec.* **2016**, *3*, 1518-1530; c) J. E. Anthony, *Angew. Chem., Int. Ed.* **2008**, *47*, 452-483; d) J. B. Li, Q. C. Zhang, *Synlett.* **2013**, *24*, 686-696; e) X. L. Shi, C. Y. Chi, *Chem. Rec.* **2016**, *16*, 1690-1700; f) C. Tonshoff, H. F. Bettinger, *Chem. Eur. J.* **2021**, *27*, 3193-3212; (g) Z. Zhang, Q. Zhang, *Mater Chem Front,* **2020**, *4*, 3419-3432.

(2) a) T. J. Ren, M. S. Song, J. W. Zhao, W. Y. Wang, X. X. Shen, C. Gao, P. Y. Yi, J. C. Xiao, *Dyes Pigm.* **2016**, *125*, 356-361; b) B .Yang, J. F. Zhao, Z. P. Wang, Z. L. Yang, Z. Q. Lin, J. W. Li, L. H. Xie, Z. F. An, H. M. Zhang, J. N. Wen, W. Huang, *Chin. Chem. Lett.* **2019**, *30*, 1969-1973; c) Z. Z. Wang, J. F. Li, S. M. Zhang, Q. Wang, G. L. Dai, B. Q. Liu, X. L. Zhu, C. Kolodziej, C. McCleese, *Chem. Eur. J.* **2018**, 24, 14442-14447; D) X. Xiao, T. R. Hoye, *Nat. Chem.* **2018**, *10*, 838-844.

(3) a) D. J. Gundlach, J. E. Royer, S. K. Park, S. Subramanian, O. D. Jurchescu, B. H. Hamadani, A. J. Moad, R. J. Kline, L. C. Teague, O. Kirillov, C .A. Richter, J. G. Kushmerick, L. J. Richter, S. R. Parkin, T. N. Jackson,J. E. Anthony, *Nat. Mater.* **2008**, *7*, 216-221; b) J. Zhang, C. Y. Wang, G. L. Long, N. Aratani, H. Yamada, Q. C. Zhang, *Chem. Sci.* **2016**, *7*, 1309-1313; c) J. L. Wang, M. Chu, J. X. Fan, T. K. Lau, A. M. Ren, X. H. Lu, Q. Miao. *J. Am. Chem. Soc.* **2019**, *141*, 3589-3596; d) X. J. Yang, X. L. Shi, N. Aratani, T. P. Goncalves, K. W. Huang, H. Yamada, C. Y. Chi, Q. Miao, *Chem. Sci.* **2016**, *7*, 6176-6181.

(4) a) L. Ahrens, J. Butscher, V. Brosius, F. Rominger, J. Freudenberg, Y. Vaynzof, U. H. F. Bunz, *Chem. Eur. J.* **2019**, *26*, 412-418; b) X. P. Wang, X. Y. Liu, R. Tom, C. Cook, B. Schatschneider, N. Marom, *J. Phy. Chem. C* **2019**, *123*, 5890-5899. c) W. Chen, X. Yang, G. Long, X. Wan, Y. Chen, Q. Zhang, *J. Mater. Chem. C* **2015**, *3*, 4698-4705; d) T. Okamoto, T. Suzuki, H. Tanaka, D. Hashizume, Y. Matsuo, *Chem. Asian J.* **2012**, *7*, 105-111; e) M. J. Sung, J. Hong, H. Cha, Y. Jiang, C. E. Park, J. R. Durrent, T. K. An, S. K. Kwon, Y. H. Kim, *Chem. Eur. J.* **2019**, *25*, 12316-12324.

(5) a) Q. Miao, T. Q. Nguyen, T. Someya. *J. Am. Chem. Soc.* **2003**, *125*, 10284-10287; b) J. B. Li , Y. B. Zhao, J. Lu, J. P. Zhang, Y. Zhao, X. M. Sun, Q. C. Zhang, *J. Org. Chem.* **2015**, *80*, 109-113; c) S. S. Zade, M. Bendikov, *J. Phys. Org. Chem.* **2012**, *25*, 452-459; d) I. Kaur, M. Jazdzyk, N. N. Stein, P. Prusevich, G. P. Miller, *J. Am. Chem. Soc.* **2010**, *132*, 1261-1263; (e) P. Gu, Z. Wang, Q. Zhang, *J. Mater. Chem. B* **2016**, *4,* 7060 – 7074; (f) P. Gu, N. Wang, A. Wu, Z. Wang, M. Tian, Z. Fu, X. W. Sun, Q. Zhang, *Chem. Asian J.* **2016**, *11*, 2135–2138.

(6) a) W. Jiang, Y. Li, Z. H. Wang, *Chem. Soc. Rev.* **2013**, *42*, 6113−6127; b) X. Y. Wang, J. Y. Wang, J. Pei, *Chem. - Eur. J.* **2015**, *21*, 3528−3539; c) M. Stolar, T. Baumgartner, *Chem. - Asian J.* **2014**, *9*, 1212−1225; d) H. M. Qu, C. Y. Chi, *Curr. Org. Chem.* **2010**, *14*, 2070−2108; e) K. Nishimur, K. Hirano, M. Miura, *Org. Lett.* **2020**, *22*, 3185-3189. f) C. Y. Huang, X. F. Liao, K. Gao, L. J. Zuo, F. Lin, X. L. Shi, C. Z. Li, H. B. Liu, X. S. Li, F. Liu, Y. W. Chen, H. Z. Chen, A. K. Y. Jen, *Chem. Mater.* **2018**, *30*, 5429-5434.

(7) a) U. H. F. Bunz, J. Freudenberg, *Acc. Chem. Res.* **2019**, *52*, 1575-1587; b) J. B. Li, Q. C. Zhang, *ACS Appl. Mater. Interf.* **2015**, *51*, 28049-28062; c) Q. Miao, *Adv. Mater.* **2014**, *26*, 5541-5549. d) A. H. Endres, M. Schaffroth, F. Paulus, H. Reiss, H. Wadepohl, F. Rominger, R. Kramer, U. H. F. Bunz, *J. Am. Chem. Soc.* **2016**, *138*, 1792-1795; e) L. Ahrens, J. Butscher, V. Brosius, F. Rominger, J. Freudenberg, Y. Vaynzof, U. H. F. Bunz, *Chem. Eur. J.* **2020**, *26*, 412-418; f) G. Li, Y. C. Wu, J. K. Gao, C. Y. Wang, J. B. Li, H. C. Zhang, Y. Zhao, Y. L. Zhao, Q. C. Zhang, *J. Am. Chem. Soc.* **2012**, *134*, 20298-20301; g) C. Y. Wang, J. Zhang, G. K. Long, N. Aratani, H. Yamada, Y. Zhao, Q. C. Zhang, *Angew. Chem. Int. Ed.* **2015**, *54*, 6292-6296; h) B. L. Hu, C. B. An, M. Wagner, G. Ivanova, A. Ivanova, M. Baumgarten, *J. Am. Chem. Soc.* **2019**, *141*, 5130-5134; i) G. J. Richards, J. P. Hill, T. Mori, *Org. Biomol. Chem.* **2011**, *9*, 5005-5017; j) S. Hahn, F. L. Geyer, S. Koser, *J. Org. Chem.* **2016**, 18, 8485-8494; k) Q. Zhao, Y. H. Li, Z. P. Wang, J. F. Wang, B. H. Yan, Y. Yu, J. W. Li, J. Y. Lin, J. F. Zhao, J. N. Wang, X. H. Zhao, Y. Q. Gao, W. Huang, *Dyes Pig.* **2019**, *170*, 107616; L) K. Z. Zhao, F. Yu, W. B. Liu, Y. J. Huang, A. A. Sadi, Y. Li, Q. C. Zhang, *J. Org. Chem.* **2020**, *85*, 101-107; (m) G. Li, K. Zheng, C. Wang, K. S. Leck, F. Hu, X. W. Sun, Q. Zhang, *ACS Appl. Mater. interface* **2013**, *5* (14), 6458–6462; (n) P. Gu, Y. Zhao, J. He, J. Zhang, C. Wang, Q. Xu, J. Lu, X. Sun, Q. Zhang, *J. Org. Chem.* **2015**, *80*, 3030-3035.

(8) a) L. Xu, H. Zhu, G. K. Long, J. Zhao, D. S. Li, R. Ganguly, Y. X. Li, Q. H. Xu, Q. C. Zhang, *J. Mater, Chem. C* **2015**, *3*, 9191-9196; b) X. L. Yu, J. Q. Wan, C. Q. Yuan, N. Guo, Y. Q. Shen, J. B. Li, *Dyes Pigm.* **2019**, *161*, 130-136. c) L. Xu, J. Z. Zhang, L. F. Yin, X. T. Long, W. Y. Zhang, Q. C. Zhang, *J. Mater. Chem. C* **2020**, *8*, 6342-6349; D) G. Li, S. Wang, S. Yang, G. Liu, P. Hao, Y. Zheng, G. Long, D. Li, Y. Zhang, W. Yang, L. Xu, W. Gao, Q. Zhang, G. Cui, B. Tang, *Chem. Asian J*. **2019,** *14*, 1807-1813.

(9) a) C. Ren, S. Y. Xiao, J. Z. Li, L. Ma, R. Chen, C. X. Ye, Y. Gao, C. L. Su, T. C. He, *Chem. Asian J.* **2021**, *16*, 309-314; b) J. M. Chen, T. J. Fan, Z. J. Xie, Q. Q. Zeng, P. Xue, T. T. Zheng, Y. Chen, X. L. Luo, H. Zhang, *Biomater.* **2020**, *237*, 119827-119834.

(10) a) S. Kawata, Y. Kawata, *Chem. Rev.* **2000**, *100*, 1777-1788; b) L. Cao, L. Xu, D. F. Zhang, Y. C. Zhou, Y. S. Zheng, Q. R. Fu, X. F. Jiang, F. S. Lu, *Chem. Phy. Lett.* **2017**, *682*, 133-139; C) J. Yu, Y. Cui, C. D. Wu, Y. Yang, B. Chen, G. Qian, *J. Am. Chem. Soc.* **2015**, *137*, 4026-4029.

(11) G. S. He, J. Zhu, A. Baev, M. Samoc, D. L. Frattarelli, N. Watanabe, A. Facchetti, H. Agren, T. J. Marks, P. N. Prasad, *J. Am. Chem. Soc.* **2011**, *133*, 6675-6680.

(12) Y. Gao, G. Feng, T. Jiang, C. Goh, L. Ng, B. Liu, B. Li, L. Yang, J. Hua, H. Tian, *Adv. Funct. Mater.* **2015**, *25*, 2857-2866.

(13) a) A. L. Appleton, S. B. Miao, S. M. Brombosz, M. Scott, N. J. Berger, S. Barlow, S. R. Marder, B. M. Lawrence, K. L. Hardcastle, U. H. F. Bunz, *Org. Lett.* **2009**, *11,* 5222-5225; b) J. B. Li, J. W. Miao, G. K. Long, J. Zhang, Y. Li, R. Ganguly, Y. Zhao, Y. Liu, B. Liu, Q. C. Zhang, *J. Mater. Chem. C* **2015**, *3*, 9877-9884.

(14) a) D. Xia, X. Y. Wang, X. Guo, *Cryst. Growth Des.* **2016**, *16*, 7124-7129; b) D. Cagardová, M. Michalík, P. Poliak, *J. Mol. Struct.* **2019**, *1175*, 297-306.

(15) a) S. Hahn, J. Butscher, Q. An, *Chem. Eur. J.* **2019**, *25*, 7285-7291. b) A. L. AppletonL, S. M. Brombosz, S. Barlow, J. S. Sears, J. L. Bredes, S. R. Marder, U. H. F. Bunz, Nat Commun **2010**, *7*, 91.

(16) G. Antonicelli, C. Gozalvez, A. Atxabal, *Org. Lett.* **2016**, *18*, 4694-4697.

(17) a) J. D. Warren, V. J. Lee, R. B. Angier, *J. Heterocyc. Chem.* **1979**, *16,* 1617-1624; b) J. Hu, D. Zhang, F. W. Harris, *J. Org. Chem.* **2005**, *70*, 707-708.

(18) D. L. Benjamin, P. Fabian, L. A. Anthony, S. Manuel, U. E. Jens, M. S. Korwin, T. Olena, R. Frank, H. Manuel, U. H. F. Bunz, *J. Mater. Chem. C* **2014**, 9609-9612.

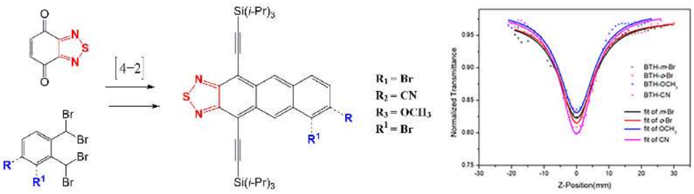
(19) L. Yuan, Y. Xiang,C. H. Liu, J. P. Wang, M .X. Fan, L. Yang, X. L. Yu , J. B. Li, *J. Lumin.* **2019**, *215*, 116690.

(20) M. X. Fan, Y. Q. Shen, Y. S. Zheng, X. L. Yu, M. Li, L. Xu, J. P. Wang, L. Yang, J. B. Li, *Chemistryselect* **2019**, *4*, 2810-2814.

(21) a) A. D. Becke, *J. Chem. Phys.* **1996**, *104*, 1040-1046; b) R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*,165-169; c) G. A. Petersson, A. Bennett, T. G. Tensfeldt, M. A. Al-Laham, W. A. Shirlety, J. J. Mantzaris, *Chem. Phys.* **1988**, *89*, 2193-2218.

(22) L. Xu, W. J. Lin, B. B. Huang, J. Z. Zhang, X. T. Long, W. Y. Zhang, Q. C. Zhang, *J. Mater. Chem. C* **2021**, 9,1520-1536.

Entry for the Table of Contents



Here, by using a simple [4+2] cycloaddition reaction between a, a, a’, a’-tetrabromo o-xylenes derivatives and benzo[c][1,2,5]thiadiazole-4,7-dione, the substituted anthrathiadiazoles with -Br, -CN, and -OCH_3 groups could be easily constructed. The as-obtained compounds display the two-photon absorption, where their cross-section values are strongly affected by the nature, position and strength of the substituted groups.