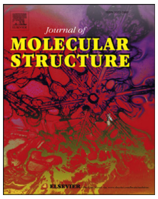
Journal of Molecular Structure 1177 (2019) 9–15

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc



Understanding the solid-state emission of a trio of 1,4-diaryl-1,3-butadiynes in terms of their molecular structure and crystal packing interactions

Michael San Angelo [a], Domarin Khago [b], Brandon Choi [a], Frank R. Fronczek [c], Ralph Isovitsch [a], *

[a] Department of Chemistry, Whittier College, Whittier CA 90601, USA
[b] National Cancer Institute, Center for Cancer Research, Structural Biophysics Laboratory, Frederick MD 21702, USA
[c] Department of Chemistry, Louisiana State University, Baton Rouge LA 70803, USA

ARTICLE INFO

Article history:
Received 1 June 2018
Received in revised form
12 September 2018
Accepted 13 September 2018
Available online 18 September 2018

Keywords:
1,4-Diaryl-1,3-butadiynes
X-ray structures
Crystal packing interactions
Solid-state absorption and emission

ABSTRACT

A trio of 1,4-diaryl-1,3-butadiynes with methoxy and trifluoromethoxy substituents in the 4- and 4′-positions were prepared in useful yields (42% for one, 95+% for the others), their structures determined and their purity ascertained. Analysis of the single crystal X-ray data for the three compounds revealed that two were mostly planar with small dihedral angles of 6–9° between their aryl rings, while one existed in a twisted conformation with a dihedral angle of approximately 53° between it's aryl rings. The solid-state absorption spectra of all three compounds were similar, with structured absorptions at approximately 340 nm. One of the compounds had absorption bands at 263 and 457 nm. Two of the compounds had similar emission bands with maxima that ranged from 440 to 450 nm, while the other was quite different, with a broad emission band with a maximum at 564 nm. Each of the three compounds had excited state decay traces that were fit to tri-exponential curves which yielded three lifetimes: a longer one attributed to aggregate emission, a shorter one arising from an intermolecular charge transfer transition, and a medium one that is assigned to a locally excited transition.

1. Introduction

Compounds that exhibit solid-state luminescence have proven useful in the construction of sensors [1–4] and solar cells [5–7]. For example, Sun et al. utilized a series of poly(phenyleneethynnylene) polymers and poly(phenylenevinylene) polymers to determine the presence of organic nitrated organic compounds that include nitroglycerin, nitromethane, and 2-nitrotoluene as indicators of the presence of explosives [1]. Luminescent poryphyrin-based compounds containing metal and metal oxide centers are often used as molecular sensors because of the ease at which their structure can be tailored. Porphyrins and metalloporphryins have been designed to determine the presence of organic solvents, mercury within water, and a variety of anions [3]. Yang et al. utilized a novel emissive metal-organic framework containing cadmium as a multisensitive sensor for Fe^{3+} and nitroaniline derivatives [4]. For the construction of Greener solar cells, Hao et al. exploited luminescent solid-state organic-inorganic halides containing compounds adopting a perovskite crystal structure [5]. The application of luminescent solids to many different research areas is dependent on the creation of new synthetic strategies, and the photophysical characterization of any new materials or molecules produced.

Myriad synthetic techniques have been utilized to successfully yield solid-state fluorescent compounds. One such example is the family of metal-catalyzed reactions that have been exploited in the production of 1,4-diaryl-1,3-butadiynyl derivatives [8–10]. Wei et al. analyzed and critiqued a variety of synthesis techniques for the successful production of symmetrical 1,3-butadiyne derivatives: oxidative coupling of terminal alkyne derivatives, modifications of Glaser-Eglinton-Hay coupling reactions, oxidative Glaser-Eglinton-Hay coupling, symmetrical diyne synthesis, and reductive palladium coupling that forms symmetrical diynes [8]. A Greener protocol utilized copper and cobalt as recyclable catalysts within ionic solvents to produce 1,4-diaryl-1,3-butadiynyl

---

* Corresponding author. 13406 Philadelphia Street, Department of Chemistry, Whittier College, Whittier CA 90601, USA.
E-mail address: risovitsch@whittier.edu (R. Isovitsch).

https://doi.org/10.1016/j.molstruc.2018.09.041

derivatives efficiently [9]. Another Green protocol used a SBA-15, a mesosporous silica, in the presence of a Cu(II) catalyst to carry out an effective coupling of phenyl acetylene [10]. Although successful synthesis protocols for symmetrical butadiynyl derivatives are legion, the synthesis of unsymmetrical butadiynyl derivatives is more challenging and often resulting in decreased percent yields [8].

The increasing ease of preparation of 1,4-diaryl-1,3-butadiynyl derivatives and their ability to form unique rigid structures in the solid-state have led to an increased interest in the study of their solid-state photophysical properties [8]. Fu et al. studied the solid-state photophysics of aromatic butadiynyl derivatives containing a BODIPY core (a conjugated aromatic ring containing fluorine, nitrogen and boron) allowing for a greater understanding of borane-BODIPY dye synthesis [2]. Pati et al. studied the solid-state photophysics of 1,3-butadiyne bridged derivatives with size varying polycyclic aromatic hydrocarbon (PAH) moieties. Both red and blue shifted emission was observed as a result of the varying PAH substituents [11]. The solid-state photophysics of 1,4-diaryl-1,3-butadiynes can often be understood in terms of the crystal packing interactions a certain molecule forms [11,12].

The overarching goal of our research is the investigation of luminescent compounds and their application in sensor construction. Toward our research goal, we have synthesized a trio of 1,4-diaryl-1,3-butadiynes with symmetric and asymmetric combinations of $-OCH_3$ and $-OCF_3$ substituents in the *para*-positions of the aryl rings. The effect of these strong electron-withdrawing and -donating substituents on the solid state luminescence of these compounds was then thoroughly investigated using steady-state and time-resolved spectroscopic techniques. The observed photophysical properties were then rationalized in terms of the structure of these compounds, and the crystal packing interactions that each experiences.

2. Experimental

2.1. General methods, materials, and instruments

Standard synthetic procedures were utilized for the preparation of compounds **1**, **2**, and **3** [13]. All reagents and solvents were obtained from Sigma-Aldrich and used without alteration. ^{1}H-, ^{13}C-, and ^{19}F NMR spectra were obtained from DMSO-d_6 solutions using a Bruker AVANCE III 600 MHz spectrometer. The ^{1}H, ^{13}C NMR spectra were referenced to TMS and the ^{19}F NMR spectra were referenced to trifluoroethanol. GC-MS data was obtained from dilute cyclohexane or dichloromethane solutions of compounds **1**–**3** using an Agilent Techologies 6890N GC system with a 5973N mass selective detector. Melting points were obtained using open capillary tubes and are not corrected. IR spectra were obtained using an ATR attachment on a Perkin-Elmer Spectrum Two FT-IR spectrometer. PXRD spectra were obtained from a Rigaku MiniFlex II XRD. Elemental analyses were done by M-H-W Laboratories of Tucson, Arizona USA.

Absorption spectra were measured from a thin layer of crystals of compounds **1**–**3** adhering to a quartz slide through static interaction (see Figure S2) using a Perkin Elmer Lambda 35 double beam UV/Visible spectrophotometer. Emission spectra were obtained from crystals of **1**–**3** packed lightly into a quartz tube using a HoribaJobinYvon FluoroMax-4 fluorometer. All emission spectra were corrected for detector response using a correction curve supplied by the fluorometer manufacturer.

Excited state lifetimes were measured from crystals of **1**–**3** lightly packed into a quartz tube using a HoribaJobinYvon TCSPC apparatus with excitation from a pulsed LED laser at 328 nm. Decay curves were analyzed using a multiexponential decay analysis program provided by the instrument manufacturer. The quality of the fitted decay curves was assessed using three criteria: plots of the residuals displaying the least oscillation and varied no more than three standard deviations; chi-squared values that were less than 1.2; and visual inspection of the goodness-of-fit between the experimental and fitted decay curves [14].

2.2. Crystallographic data acquisition and refinement

Colorless needle fragments of **1** ($0.51 \times 0.23 \times 0.15$ mm) and **2** ($0.50 \times 0.43 \times 0.25$ mm) were used for data collection at $T = 170$ K for **1** and $T = 100$ K for **2** on a Bruker Kappa APEX-II DUO diffractometer equipped with an Oxford Cryosystems Cryostream chiller and graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods, and structure refinements were carried out by *SHELXL2014/7* [15]. All hydrogen atom locations were inferred from neighboring sites.

2.3. Synthesis of 1,4-bis(4-trifluoromethoxyphenyl)buta-1,3-diyne (1)

4- (Trifluoromethoxy)phenylacetylene (0.500 g, 2.69 mmol), CuCl (0.050 g, 0.51 mmol), and *N*, *N*, *N'*, *N'*-tetramethylethylenediamine (TMEDA) (10 drops) were added to 2-propanol (200 mL), which was then refluxed gently for 45 min until it turned green. The 2-propanol was then evaporated to yield thick green paste. HCl (approximately 40 mL of a 0.6 M solution) was then used to wash the green paste until a white solid resulted, which was collected over vacuum filtration, washed with an excess of water, and then air dried. 0.49 g (98%) of pure **1** was obtained as an off-white solid.

M.p.: 102–104 °C. $R_f = 0.22$ (silica, light petroleum ether). IR (ATR): 2144, 1502, 1154 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d_6): 7.77 (d, $^3J = 12.0$ Hz, 4 ArH); 7.44 (d, $^3J = 6.01$ Hz, 4 ArH). ^{13}C NMR (150 MHz, DMSO-d_6): 149.57; 135.16; 121.95; 120.02; 119.52; 81.18; 74.49. ^{19}F NMR (600 MHz, DMSO-d_6): 21.66. GC-MS: 370.1 ($[M]^+$, $C_{18}H_8O_2F_6^+$; calc. 370.3). *Anal.* Calcd. for $C_{18}H_8F_6O_2$: C, 58.39; H, 2.18. Found: C, 58.51; H, 2.43.

2.4. Synthesis of 1-(4-trifluoromethoxyphenyl)-4-(4-methoxylphenyl)buta-1,3-diyne (2)

4-(Trifluoromethoxy) phenylacetylene (0.352 g, 1.89 mmol), 4-ethynylanisole (0.250 g, 1.89 mmol), CuCl (0.051 g, 0.51 mmol), and TMEDA (10 drops) were added to 2-propanol (200 mL), and then gently refluxed for 45 min to yield a green solution. The 2-propanol was then evaporated to yield a thick green paste. HCl (approximately 40 mL of a 0.6 M solution) was then used to wash the green paste until an off-white solid resulted, which was collected over vacuum filtration, washed with an excess of water, and then air-dried. 0.250 g of light beige crystals of pure **2** (42%) was isolated on a silica column using a cyclohexane mobile phase.

M.p.: 96–98 °C. $R_f = 0.72$ (silica, cyclohexane). IR (ATR): 2919, 2217, 2150, 1500 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d_6): 7.75 (d, $^3J = 6.0$ Hz, 2 ArH); 7.58 (d, $^3J = 12.0$ Hz, 2 ArH); 7.01 (d, $^3J = 12.0$ Hz, 2 ArH); 7.44 (d, $^3J = 12.0$ Hz, 2 ArH); 3.81 (s, CH_3). ^{13}C NMR (150 MHz, DMSO–d_6): 161.07; 149.31; 149.29; 134.93; 121.92; 120.53; 119.53; 115.12; 112.36; 83.24; 80.14; 75.20; 72.60, 55.88. ^{19}F NMR (600 MHz, DMSO-d_6): 21.66. GC-MS: 316.2 ($[M]^+$, $C_{18}H_{11}O_2F_3^+$; calc. 316.3). *Anal.* Calcd. for $C_{18}H_{11}O_2F_3$: C, 68.35; H, 3.51. Found: C, 68.55; H, 3.79.

2.5. Synthesis of 1,4-bis(4-methoxyphenyl)buta-1,3-diyne (3)

4-Ethynylanisole (0.680 g, 5.15 mmol), CuCl (0.068 g, 0.69 mmol), and TMEDA (10 drops) were added to 2-propanol (10