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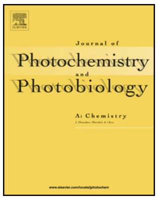

Tunable molecular configuration for significant enhancement of two-photon absorption based on novel octupolar benzoimidazole derivatives

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ABSTRACT

Two novel octupolar molecules including benzoimidazole electron-accepting (A) branches and a triphenylamine electron-donating (D) center have been synthesized and characterized (p-ETBN and m-ETBN). Their photophysical and photochemical properties were investigated systematically including single-photon absorption, two-photon absorption (2PA) and charge transfer performance. Their 2PA properties have been investigated by the open aperture Z-scan technique, and the values of the 2PA cross section at 800 nm for p-ETBN and m-ETBN are ~300 GM and ~100 GM, respectively. Interestingly, both of them have the same D, A and π-conjugating units with only the different molecular configuration, the 2PA response of them differs by almost three times, which are found to be the different excited-state dipole moments and intramolecular charge-transfer. Our results reveal a new rule of molecular design for obtaining some excellent 2PA materials for their potential biophotonic and optoelectronic applications.

1. Introduction

Octupolar molecules have been attracting extensively attention owing to their structural symmetry and excellent optical and electronic properties in the past decades [1]. With well-defined structures and suitable conjugated length, they have considerably extended the possibilities of molecular engineering of nonlinear optical molecules by enlarging the dimensionality of the charge transfer [2].

Two-photon absorption (2PA) is a third-order nonlinear optical process involving simultaneous absorption of two low-energy photons to reach the high-energy excited state, which can be applied in many areas including optical limiting [3], two-photon fluorescence excitation microscopy [4], 3D optical data storage [5], two-photon upconversion lasing [3b,6], and photodynamic therapy [7]. Recently, much interest has been focused on the design and synthesis of organic molecules with large 2PA cross sections [8], and theoretical and experimental studies on the relationship between structure and 2PA properties have also been widely investigated [9].

Benzoimidazole-based compounds have been demonstrated showing good electrical and optical properties due to high electron affinity and special structures, which have been extensively used to some fields of optoelectronic devices such as organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs) and organic photovoltaics (OPVs) [10]. However, up to now, this unit had attracted only scant attention for the nonlinear optical properties. In particular, octupolar molecules consisting of some benzoimidazole electron-accepting (A) branches and an electron-donating (D) center linked through π-conjugated because of the good steric configuration of the conjugated system, strong intramolecular charge-transfer (ICT), and additional cooperative enhancement between the centers [11]. The lack of interest is surprising because, owing to their twisted symmetries, these compounds might exhibit significant nonlinear optical activities when the electron-attracting benzoimidazole branches are symmetrically decorated with the electron-donating centers.

Triphenylamine and their derivatives, as the important electron-donating centers to construct octupolar D–π–A molecules, have attracted great interest owing to their superior electron-donating properties [2d,12]. However, to the best

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of our knowledge, benzoimidazole octupolar molecules using triphenylamine as center, showing enhancement of two-photon absorption with tunable molecular configuration in femotosecond timescales, have still been reported very few during the past decades. Given that such octupolar structures might present good activities for special nonlinear optical properties, we designed and synthesized two isomeric octupolar D–π–A molecules, named p-ETBN and m-ETBN, which contains three benzoimidazole units as branches and one triphenylamine unit as center. Their nonlinear optical properties were studied systematically. It is particularly intriguing to compare the 2PA properties of p-ETBN and m-ETBN, both have the same D, A and π-conjugating units. When changed their molecular configuration, they exhibit an identical 2PA properties, the 2PA response of them differs by almost three times. The DFT computations were conducted to unravel their electronic structures and to rationalize their NOL properties. We wish to modify the photophysical properties of the compounds by changing the molecular configuration and obtain some excellent 2PA materials and to further understand the structure–property relationship.

2. Experimental

2.1. Materials and characterization

Tris(4-bromophenyl)amine, ethynyltrimethylsilane, bis(triphenylphosphine) palladium(II) chloride were purchased from *Tokyo Chemical Industry Co., Ltd*. Cuprous iodide (CuI), dimethyl formamide (DMF), triethylamine (NEt_3) were obtained from J&K Chemical company. All other reagents were from Sinopharm Chemical Reagent Co. Ltd. The solvents were dried using standard procedures. All other reagents were used as received from commercial sources, unless otherwise stated. ^1H NMR and ^{13}C NMR spectra were determined in $CDCl_3$ with a Bruker DRX 400 MHz spectrometer. Chemical shifts (*d*) were given relative to tetramethylsilane (TMS). MALDI-TOF mass spectra were recorded on a Shimadzu/Krotos Axima CFR in the linear mode using a laser ($\lambda = 337$ nm). Fluorescent and UV–vis spectra of these derivatives were measured with a FLSP920 and HITACHI U3010 spectrophotometers. Tris(4-((trimethylsilyl)ethynyl)phenyl)amine (**1**), tris(4-ethynylphenyl)amine (**2**), 2-(4-bromophenyl)-1-phenyl-1H-benzo[d]imidazole (**3**), and 2-(3-bromophenyl)-1-phenyl-1H-benzo[d]imidazole (**4**) were synthesized following the method reported in the literature [13].

2.2. Synthesis of compound tris(4-((4-(1-phenyl-1H-benzo[d]imidazol-2-yl)phenyl) ethynyl)phenyl)amine (p-ETBN)

A 20 mL flask was charged with tris(4-ethynylphenyl)amine **(2)** (0.317 g, 1 mmol), 2-(4-bromophenyl)-1-phenyl-1H-benzo[d]imidazole **(3)** (1.396 g, 4 mmol), PPh_3 (0.104 g, 10%), CuI (0.076 g, 10%) and $Pd(PPh_3)_2Cl_2$ (0.140 g, 5%). The mixture was degassed and backfilled with argon before injecting dried NEt_3 (4 mL) and dried DMF (7.5 mL). The mixture was sealed with a rubber septum and heated to 60 °C for 30 h, then quenched with NH_4Cl and extracted with $CHCl_3$. The organic layer was washed with brine for 2 times and dried over $MgSO_4$ before the solvents was evaporated in vacuum. The residue was purified with column chromatography on silica gel using dichloromethane:hexane (10:1) as eluent to give a yellow solid of **p-ETBN**. Yield: 0.58 g, 52%. ^1H NMR (400 MHz, $CDCl_3$): 7.98–7.92 (m, 3H), 7.57 (br, 6H), 7.57–7.54 (m, 9H), 7.46–7.44 (d, 6H, *J* = 7.62 Hz), 7.41–7.39(d, 9H, *J* = 8.50 Hz), 7.34 (br, 9H), 7.27–7.24 (m, 3H), 7.06–7.04 (6H, *J* = 6.07 Hz), ^{13}C NMR (100 MHz, $CDCl_3$): 151.5, 162.5, 146.8, 142.4, 137.1, 136.7, 132.9, 131.4, 130.1, 142.7, 123.8, 123.4, 119.7, 117.7, 110.6, 91.4, 88.9. MALDI-TOF mass: 1122.5 (M^+).

2.3. Synthesis of compound tris(4-((3-(1-phenyl-1H-benzo[d]imidazol-2-yl)phenyl) ethynyl)phenyl)amine (m-ETBN)

A 20 mL flask was charged with tris(4-ethynylphenyl)amine **(2)** (0.317 g, 1 mmol), 2-(3-bromophenyl)-1-phenyl-1H-benzo[d]imidazole **(4)** (1.396 g, 4 mmol), PPh_3 (0.104 g, 10%), CuI (0.076 g, 10%) and $Pd(PPh_3)_2Cl_2$ (0.140 g, 5%). The mixture was degassed and backfilled with argon before injecting dried NEt_3 (4 mL) and dried DMF (7.5 mL). The mixture was sealed with a rubber septum and heated to 60 °C for 30 h, then quenched with NH_4Cl and extracted with $CHCl_3$. The organic layer was washed with brine for 2 times and dried over $MgSO_4$ before the solvents was evaporated in vacuum. The residue was purified with column chromatography on silica gel using dichloromethane:hexane (10:1) as eluent to give a yellow solid of m-ETBN. Yield: 3.93 g, 35%. ^1H NMR (400 MHz, $CDCl_3$): 7.94–7.90 (t, 6H, *J* = 8.22 Hz), 7.56–7.48 (m, 12H), 7.41–7.27 (m, 12H), 7.35–7.33 (d, 6H, J = 7.00 Hz), 7.32–7.22 (m, 9H), 7.08–7.06 (d, 6H, *J* = 7.87 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 151.4, 146.7, 142.7, 137.1, 136.6, 132.9, 132.3, 130.2, 129.9, 128.7, 128.2, 127.4, 124.0, 123.6, 123.3, 119.9, 117.7, 90.0, 88.5. MALDI-TOF mass: 1122.2 (M^+).

2.4. Z-scan and pump-probe measurements

The laser pulses were produced by a mode-locked Ti:Sapphire laser (Quantronix, IMRA), which seeded a Ti:Sapphire regenerative amplifier, and focused onto a 1-mm-thick quartz cuvette containing the solutions of the derivatives. The incident and transmitted laser pulse energy were monitored by moving the cuvette along the propagation direction of the laser pulses. The Z-scan experimental system was calibrated using a piece of cadmium sulfide (CdS) bulk crystal as a reference because it possesses large 2PA at the wavelength of 780 nm and has been well investigated in our laboratory. The 2PA coefficient of CdS was determined to be 6.4 ± 0.6 cm GW^{-1}, which was in good agreement with theoretical values within the experiment uncertainty [14].

3. Results and discussions

3.1. Synthesis

Scheme 1 shows the molecular structures and synthetic route of p-ETBN and m-ETBN. It can be seen the molecules contain a triphenylamine center and three benzimidazole branches by linking with the alkynyl groups. Our design of the benzimidazole-type octupolar molecules of p-ETBN and m-ETBN was inspired by the structure of benzimidazole derivatives, a widely used material for fluorescent OLEDs that exhibits high electron mobility and twisted structures. Moreover, the benzimidazole-type octupolar molecules are limited. To expand the family of benzimidazole, a poorly conjugating C≡C is introduced between the benzimidazole and the triphenylamine groups to inhibit the intramolecular charge transfer (ICT), which has been demonstrated to enhance the 2PA [15]. The key intermediate for the synthesis of p-ETBN and m-ETBN was tris(4-ethynylphenyl)amine (**2**), which was synthesized by Sonogashira couplings of tris(4-bromophenyl)amine and ethynyltrimethylsilane using $Pd(PPh_3)_2Cl_2$ and CuI as catalysts. The 2-(4-bromophenyl)-1-phenyl-1H-benzo[d]imidazole (**3**) and 2-(3-bromophenyl)-1-phenyl-1H-benzo[d]imidazole (**4**) were synthesized according to the literature procedures. Further reaction with compounds **2** and **3** or **4** in refluxing dimethyl formamide/triethylamine (15:8, v/v) affords the octupolar molecules