



Effect of the mismatch structure on crystal packing, physical properties and third-order nonlinearity of unsymmetrical twistacenes



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ABSTRACT

A novel family of unsymmetrical twistacene analogues were synthesized in a palladium-promoted cross-coupling reaction and fully characterized, where five-membered ring was embedded into the main skeleton in these molecules. The formed all-carbon compounds appreciate a series of promising photophysical properties such as good thermal stability and photostability than that of acenes consisting of all six-membered rings. All of them emitted strong solution fluorescence covered a wide range from cyan to yellow. In addition, the nonlinear optical properties were further investigated through the top-hat Z-scan technique at 515 nm, which indicates that all of them presented excellent third-order nonlinear absorption effects.

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1. Introduction

The study of polycyclic aromatic hydrocarbons, particularly the linear acenes has become a fascinating research topic during the past years because these resulting all-carbon molecules, as the functional dyes and materials, can be used in organic electronics such as organic light emitting diodes, field effect transistors and photovoltaic cells [1–3]. Chow found that the fabricated OFET devices using hexacene single crystals presented the highest hole mobility of $4.28 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [4]. In addition, some of them can self assemble into nanostructures that were utilized as the probes in cell imaging and detection [5,6]. For example, Xiao and co-workers developed a three-dimensional fluorescent probe based on twistacenes with tunable emission for enhancing imaging of living cells [7]. The impetus for the wide spread interest also stemmed from the predicted optoelectronic property raised by theorists including superconductivity, ferromagnetism and open shell biradical state [8–10]. This stimulated an ongoing investigation to realize and

elucidate their electronic behaviors. However, these large acenes, usually referring to pentacene or higher ones, encountered some annoying disadvantages such as very low solubility, susceptible to light and oxygen, polymerization, which restrict the excellent performance of larger acenes in organic electronic devices.

To overcome these drawbacks, one of the methods is to incorporate the heteroatoms into the acene skeletons [11–20]. Another method is to introduce five-membered rings to replace the traditional six-membered rings [21–23]. This strategy can not only result into ease of synthesis, isolation and enhance stability, but also tune conveniently their optoelectronic properties. Haley and co-workers reported a series of substituted indeno [1,2-b]fluorene derivatives that exhibited interesting antiaromatic, ambipolar property and could be used as n-type materials [24,25]. Functionalized cyclopenta[hi]aceanthrylenes and dicyclopenta[de,mn] tetracenes observed in the group of Plunkett presented the low-lying LUMOs, being comparable to PCBM [26,27]. Wuld, Miller and Anthony groups successively synthesized a series of the higher acenes decorated with phenyl, triisopropylsilylethynyl (TIPS), arylthio substituents [28–30]. More recently, Pascal, Zhang and Xiao successfully reported some unsymmetrical and symmetrical twistacenes containing phenanthrene/pyrene unit in the terminal [31–42]. The resulting molecules showed high stability and emit

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strong fluorescence covered a wide range from blue to cyan, green and red that were used as active layer in organic emitting light diodes.

More recently, nonlinear optical (NLO) materials have attracted a growing interest because of their potential military applications such as optical switching, data storage, optical limiting and optical communication [43–47]. These materials based on organic π -conjugated compounds exhibited promising features including well-defined structural flexibility, functionality as well as strong susceptibility. Till now, using all-carbon twistacenes containing pyrene unit for non-linear behavior has rarely studied. It is generally accepted that pyrene-based materials usually showed ultrafast broadband optical response [48–50]. This stimulates us to explore the possibility.

In this work, we have synthesized and characterized four novel twistacenes (**PyN**, **PyA**, **PyPy**, **PyPh**) annulated by different units in the terminal (Scheme 1). Single crystals analysis showed that the formed molecules displayed twisted structures. We became more interested in the effect of the mismatch structure on the physical properties of unsymmetrical acenes, and thus the optoelectronic profiles were studied in detail. Moreover, the NLO behaviors of compounds **PyN**, **PyA**, **PyPy**, **PyPh** were studied through the top-hat Z-scan technique, which exhibited rapid optical response.

2. Experimental

2.1. Materials and instruments

The chemicals were purchased from J & K and Alfa Aesar companies, used directly without further purification. ^1H , ^{13}C NMR spectra were recorded on Bruker AV 600 (600 MHz for ^1H , 150 MHz for ^{13}C) spectrometer. The chemical shifts are obtained in ppm with δ of CDCl_3 (7.260 ppm in ^1H NMR). MALDI-TOF mass spectra were carried out on Bruker Biflex III MALDI-TOF. X-Ray crystallographic data were obtained with a Bruker APEX II CCD or Bruker AXS Smart-1000 diffractometer with graphite-monochromatic Mo $K\alpha$ radiation. Column chromatography was finished on silica gel (200–300 mesh). UV/vis and fluorescence spectra were measured on Shimadzu UV-2550 and RF5300PC spectrometers. The electrochemical behaviors were recorded on CHI 630 A analyzer with a standard three-electrode cell. The tests were performed in 0.1 M

tetrabutylammonium hexafluorophosphate solution (anhydrous dichloromethane) under a nitrogen atmosphere at a scan rate of 0.05 V s^{-1} . Thermogravimetric analyses (TGA) were performed using a PerkinElmer Pyris 6 under N_2 with a heating rate of $10 \text{ }^\circ\text{C/min}$.

2.2. Synthesis route

2.2.1. Synthesis of **3**

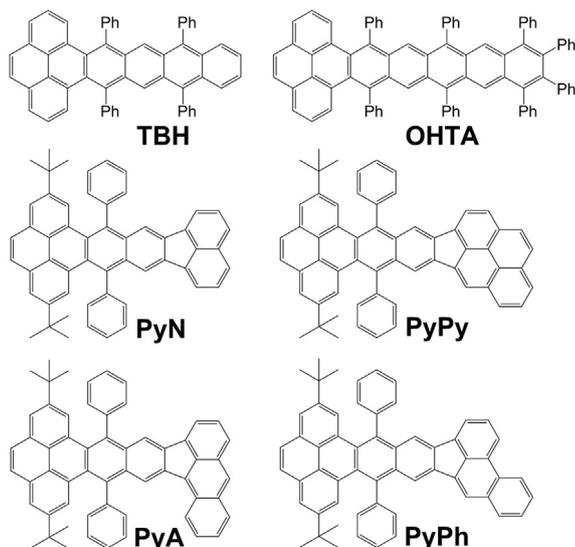
A mixture of compound **1** (760 mg, 1.05 mmol), 1-naphthylboronic acid **2** (150 mg, 0.87 mmol), $\text{Pd}(\text{PPh}_3)_4$ (61 mg, 0.052 mmol) and K_2CO_3 (2.76 g, 20 mmol) in THF/ H_2O (20 mL/10 mL, v/v, 2:1) was stirred for 24 h at $85 \text{ }^\circ\text{C}$ under nitrogen atmosphere. After cooling to room temperature, water was added. The as-formed solution was then extracted with dichloromethane (40 mL \times 3). The obtained organic phase was dried over Na_2SO_4 and concentrated in reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/dichloromethane (v/v, 50:1) as the eluent to give a mixture of **3** (345 mg, 51%). FT-IR (KBr): 3056, 2956, 2863, 1603, 1444, 883, 774, 699 cm^{-1} . ^1H NMR (600 MHz, 298 K, CDCl_3): δ = 8.247 (s, 1H), 8.18 (d, J = 1.2 Hz, 1H), 8.115 (d, J = 1.8 Hz, 1H), 7.925 (d, J = 8.4 Hz, 2H), 7.9 (s, 1H), 7.874 (d, J = 1.8 Hz, 1H), 7.861 (s, 3H), 7.73 (d, J = 7.8 Hz, 1H), 7.651–7.582 (m, 5H), 7.568–7.521 (m, 2H), 7.508–7.44 (m, 5H), 7.396 (t, J = 7.2 Hz, 1H), 7.333 (t, J = 7.2 Hz, 1H), 1.146 (s, 9H), 1.112 (s, 9H). ^{13}C NMR (150 MHz, 298 K, CDCl_3): δ = 147.54, 147.51, 142.14, 142.04, 139.49, 138.46, 136.33, 135.14, 133.50, 132.75, 132.54, 132.49, 132.38, 132.21, 131.14, 130.99, 130.76, 130.49, 130.48, 130.17, 129.82, 129.72, 129.67, 129.62, 129.52, 129.49, 129.44, 128.37, 128.34, 128.03, 127.93, 127.83, 127.79, 127.55, 127.10, 126.37, 126.25, 126.02, 125.34, 124.11, 124.05, 122.96, 122.73, 122.67, 34.94, 34.91, 31.54, 31.52. MALDI-TOF (MS): Calc. for $\text{C}_{54}\text{H}_{43}\text{Br}$: $[m/z]$ 772.3, found: $[m/z]$ 772.3.

2.2.2. Synthesis of **4**

A mixture of **3** (211 mg, 0.27 mmol), $\text{Pd}_2(\text{dba})_3$ (50 mg, 0.055 mmol), $\text{P}(\text{Cy})_3$ (61 mg, 0.22 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 1.0 mL) in dimethylacetamide (DMAc, 10 mL) was stirred at $155 \text{ }^\circ\text{C}$ under nitrogen atmosphere for 3 days. After cooling to room temperature, DMAc was evaporated under reduced pressure. Water was added to the residue, which was extracted with dichloromethane (40 mL \times 3). The combined organic layers were dried over Na_2SO_4 . After the organic solvent was removed under reduced pressure, the formed residue was purified on silica gel column with petroleum ether/dichloromethane (v/v, 50:1) to give a green solid (**4**, 144 mg, 76%). FT-IR (KBr): 3041, 2958, 2907, 2865, 1604, 1438, 886, 769, 702 cm^{-1} . ^1H NMR (600 MHz, 298 K, CDCl_3): δ = 8.33 (s, 2H), 8.17 (d, J = 1.2 Hz, 2H), 7.87–8.76 (m, 6H), 7.84 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 6.6 Hz, 4H), 7.64 (q, 6H), 7.55 (t, J = 7.2 Hz, 2H), 1.14 (s, 18H). ^{13}C NMR (150 MHz, 298 K, CDCl_3): δ = 147.39, 142.99, 137.43, 137.19, 137.05, 135.92, 132.83, 132.23, 130.71, 130.47, 130.19, 129.80, 129.48, 128.29, 127.78, 127.67, 127.08, 126.22, 125.50, 124.04, 122.34, 119.43, 119.16, 34.94, 31.58. MALDI-TOF (MS): Calc. for $\text{C}_{54}\text{H}_{42}$: $[M]$ 690.3, found: $[M]$ 690.5.

2.2.3. Synthesis of **6**

A mixture of compound **1** (403 mg, 0.56 mmol), 1-pyrenylboronic acid **5** (115 mg, 0.47 mmol), $\text{Pd}(\text{PPh}_3)_4$ (39 mg, 0.034 mmol) and K_2CO_3 (2.76 g) in THF/ H_2O (20 mL/10 mL, v/v, 2:1) was stirred for 2d at $85 \text{ }^\circ\text{C}$ under nitrogen atmosphere. After cooling to room temperature, brine (100 mL) was added. The obtained solution was extracted with dichloromethane (30 mL \times 3). The collected organic phase was dried over Na_2SO_4 and concentrated in reduced pressure. The crude product was purified by silica gel chromatography column using petroleum ether as the eluent to afford a light green solid (**6**, 272 mg, 68%). FT-IR (KBr): 3037, 2953,



Scheme 1. Chemical structures of compounds **TBH**, **OHTA**, **PyN** (**4**), **PyPy** (**7**), **PyA** (**10**) and **PyPh** (**13**).

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