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# Double [4 + 2] Cycloaddition Reaction To Approach a Large Acene with Even-Number Linearly Fused Benzene Rings: 6,9,16,19-Tetraphenyl-1.20,4.5,10.11,14.15-Tetrabenzooctatwistacene

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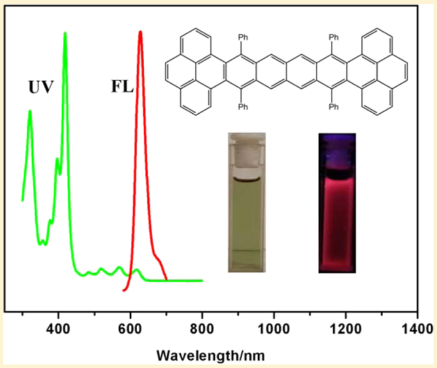
Supporting Information

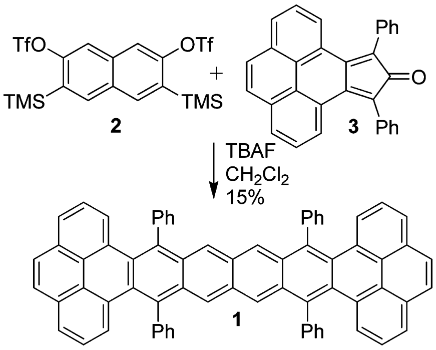
**ABSTRACT:** It is more challenging to synthesize acenes with even-number fused benzene rings (AWEB) than acenes with odd-number fused benzene rings (AWOB) because AWEB are either synthetically asymmetric or the precursors to prepare AWEB are very difficult to obtain or to prepare from commercially available sources. In this work, we employed 2,6-naphthodiyne precursor (**2**) as an effective synthon to prepare a large AWEB, 6,9,16,19-tetraphenyl-1.20,4.5,10.11,14.15-tetrabenzooctatwistacene (**1**), through a simple, one-step, double [4 + 2] cycloaddition reaction. The physical properties of as-prepared octatwistacene (**1**) have been carefully studied, and the OLED performance of compound **1** was also investigated.



## INTRODUCTION

Acenes,[1] a family of polycyclic aromatic hydrocarbons (PAHs) with linear fused benzene rings, have been widely investigated recently[2] due to their potential applications in organic optoelectronic devices such as organic field effect transistors (OFET), organic light emitting diodes (OLED), and organic photovoltaics (OPV).[3] Since the properties of acenes are heavily dependent on the number of fused benzene rings and substituted groups on their frameworks, developing simple methods to approach stable acenes (note that the acenes with more than five fused benzene rings become extremely unstable[4]) and their derivatives are highly desirable. In general, the construction of acenes with odd-number fused benzene rings (AWOB) is much easier than that with even-number fused benzene rings (AWEB) because AWOB can easily be prepared by fusing two of the same synthons together through one-step Adol condensation[5] or Diels–Alder reaction.[6,2c] More importantly, these synthons can be easily obtained or prepared from commercially available sources. However, AWEB requires more steps to prepare because they are synthetically asymmetric.[7] Generally, there are two ways to prepare AWEB: (i) a step-by-step method, for example, the synthesis of hexacene[7c,d] and octacene,[7e] and (ii) through even-number bis(aryne) synthons such as the precursor of 2,6-naphthodiyne.[8] Recently, Kitamura et al.[8] have demonstrated that 2,6-naphthodiyne precursor (**2**, Scheme 1) can be used as an effective synthon to prepare tetraacenes. Their success makes us believe that this synthon should be a powerful building block to prepare larger AWEB more concisely. Herein, we reported a concise method to prepare a new large AWEB 6,9,16,19-tetraphenyl-1.20,4.5,10.11,14.15-tetrabenzooctatwistacene (**1**) by employing this synthon (**2**). The as-prepared octatwistacene (**1**) was carefully characterized (all data have been provided in the Supporting Information), and its performance in OLED devices was also investigated.

**Scheme 1. Synthetic Route of Compound 1**



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## RESULTS AND DISCUSSION

**Synthesis and Characterization.** The synthetic route of compound **1** is shown in Scheme 1. Bis(aryne) precursor (**2**)[8] and compound **3**[9] were prepared according to the reported procedures. The targeted compound **1** was obtained in 15% yield through [4 + 2] reaction between compound **3** and in situ generated 2,6-naphthodiyne. Compound **1** is a dark-green solid with poor solubility in most common organic solvents such as $CH_2Cl_2$, $CH_3OH$, THF, and DMF. The TGA curve shows that compound **1** could be thermally stable up to 480 °C (Figure S1, Supporting Information).

The structure of compound **1** was confirmed by $^1H$ NMR, elemental analysis, and mass spectroscopy. A clear $^1H$ NMR recorded at THF-$d_8$ is shown in Figure 1. The signals observed at $\delta = 7.84$ (s, 4H), 7.78 (d, 4H), 7.66 (d, 4H), 7.21 (t, 4H) can be assigned to the protons in the pyrene unit, while the singlet peak at $\delta = 8.64$ (s, 4H) was attributed to the protons 5 residing on the acene framework. The multiple peaks (20H) between 7.53 and 7.64 are from the protons on the phenyl substituents. Attempts to obtain high quality single crystals of compound **1** for data collection failed.

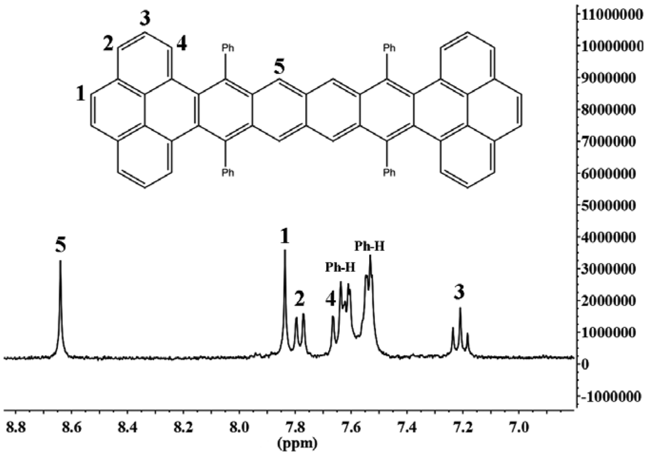

**Figure 1.** $^1H$ NMR spectrum of compound **1** in THF-$d_8$.

Figure 2 shows the UV–vis spectrum of compound **1** in 1,2-dichlorobenzene (ODCB). The longest absorption of compound **1** appears at 618 nm, which falls between that of heptatwistacene ($\lambda_{max}$ = 530 nm)[10] and nonatwistacene ($\lambda_{max}$ = 739 nm).[11] The longest absorption of compound **1** redshifts 88 nm beyond that of the shorter heptatwistacene[10] and blueshifts 121 nm beyond that of longer nonatwistacene.[11] In addition, the bands in the finger region (450–650 nm) are the characteristic of the acene family[10,11] (inset in Figure 2). Meanwhile, a red fluorescence with the emission wavelength at 628 nm is investigated. The fluorescence quantum yield of compound **1** in $CH_2Cl_2$ is nearly 10% using rhodamine B as a standard ($\Phi_f$ = 0.31 in water) (Figure 3).[12] Moreover, compound **1** could be stored in the dark as its solid form for several months, and no obvious decomposition was observed. In addition, the degassed solution of compound **1** also showed good stability for at least 3 h and no obvious changes in UV–vis spectrum after this solution was kept in the dark for 3 h (Figure S2, Supporting Information). However, compound **1** degraded very quickly under light. As shown in Figure S3 (Supporting Information), the bands in the finger region (450–650 nm) disappeared under natural light after 30 min, indicating degradation of compound **1**.

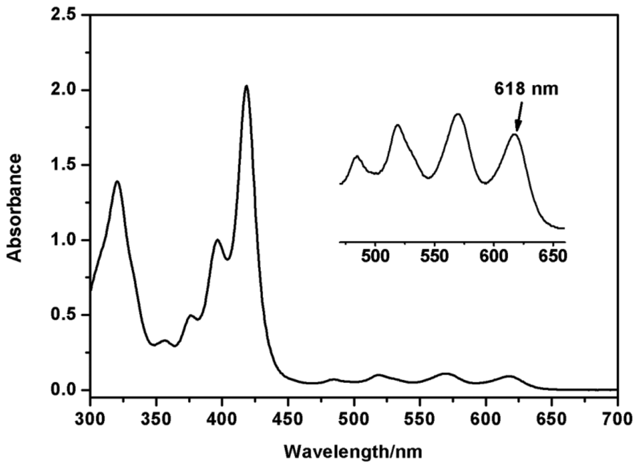

**Figure 2.** UV–vis spectrum of compound **1** in ODCB.

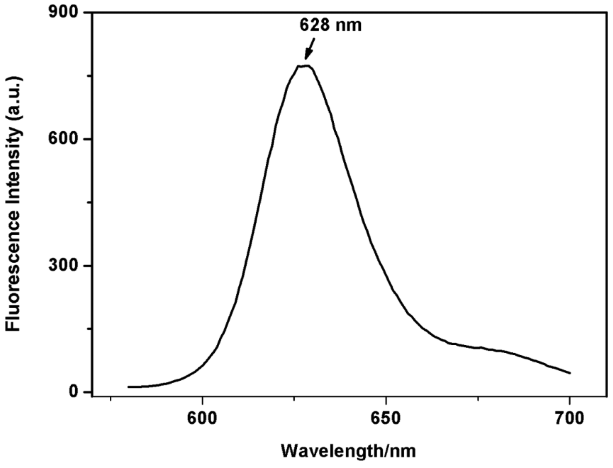

**Figure 3.** Fluorescence spectrum of compound **1** in ODCB. The excitation wavelength is 570 nm.

Cyclic voltammetry (CV) of compound **1**, measured in 0.1 M tetrabutylammonium perchlorate (TBAP)/1,2-dichlorobenzene (ODCB) (recorded at 50 °C for the low solubility), shows one reversible oxidation peak and two reversible reduction peaks (Figure 4). The half-wave reduction and oxidation potentials are located at −1.83, −2.16, and 0.26 V related to $Fc/Fc^+$, respectively. The HOMO and LUMO energies are estimated to be −5.06 and −2.97 eV, respectively, according to the equation $E_{LUMO} = -4.8\ \text{eV} - E_{red}$ and $E_{HOMO} = E_{LUMO} - E_{gap}$.[13] The bandgap calculated from the CV is 2.09 eV, which is close to the result from UV–vis absorption (2.01 eV). Moreover, the bandgap of compound **1** is between that of heptatwistacene (2.5 eV)[10] and that of nonatwistacene (1.72 eV).[11]

**Theoretical Calculation.** Density functional theory (DFT) and time-dependent density functional theory (TD-DFT) at the PBE0/6-31G (d,p) level[14] were employed to calculate the absorption wavelength in ODCB solution with the polarizable continuum model (PCM)[15] using the Gaussian 09 software package.[16] The calculated maximum absorption wavelength in ODCB solution is 641 nm (Figure S3, Supporting Information), which corresponds to the electron excitation from

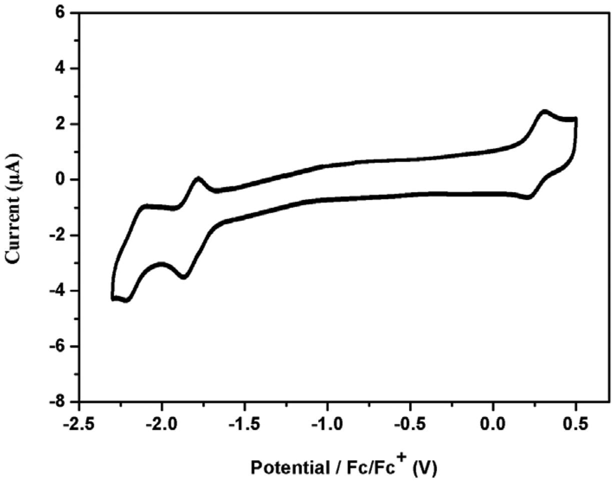

**Figure 4.** CV curve of compound **1** in ODCB.

HOMO to LUMO. The calculated vertical transition energy is 1.94 eV. It is consistent with the experimental results (2.09 eV). The optimized geometry of compound **1** at the PBE0/6-31G (d, p) level of theory is shown in Figure 5a. The calculated dihedral between pyrene unit and tetracene unit is 21.53°, which suggests that the as-prepared compound **1** should have a twisted structure. Furthermore, the wave function plots of HOMO and LUMO are shown in Figure 5b. The HOMO and LUMO are mainly contributed from the orbitals of the middle four benzene rings.

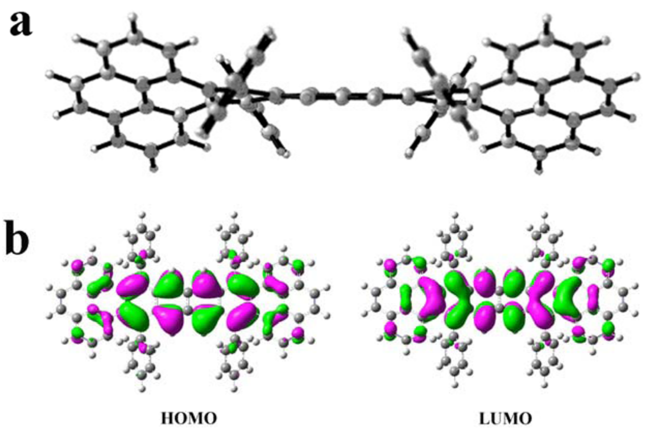

**Figure 5.** (a) Optimized geometry of compound **1** at the PBE0/6-31G (d, p) level of theory. (b) Wave function plot for the HOMO and LUMO of compound **1**.

**OLED Devices.** OLED devices with a structure of ITO/MoO$_3$(5 nm)/NPB(80 nm)/Rubrene:X wt % **1** (20 nm)/Alq$_3$(60 nm)/LiF/Al were fabricated to examine electroluminance performance of compound **1**. The concentrations of dye (**1**) were tuned from 1 wt % to 4, 8, and 15 wt %. As shown in Figure 6a, the change in dye concentration has little effect on its current density−voltage (J−V) characteristics, indicating there is no obvious charge carrier trapping effect. However, the turn-on voltage shows a small increase as the dye concentration increases, and meanwhile, the efficiencies (as shown in Figure 6b,c) decrease as the dye concentration increases, which indicates that there is obvious concentration quenching effect. The device with the lowest dye concentration of 1 wt % shows a maximum EQE, current efficiency, and power efficiency of 0.58%, 0.45 cd/A and 0.26 lm/W, respectively. Considering the PL quantum yield of 10%, the maximum EQE of 0.58% reaches the maximum theoretical value, which indicates that the device has very good electron/hole charge carrier balance. The electroluminance spectra for the four devices are shown in Figure 6d. As shown, all the four devices emit at a peak around 634 nm with a shoulder around 692 nm. However, the ratio between the peak and the shoulder shows some decrease as the concentration of the dye increases and there is also some red shift in the emission peak from 634 to 638 nm, which should be caused by the concentration quenching effect as well. The residual emission from 500 to 600 nm are due to emission from Rubrene and Alq3, which may result from inefficient energy transfer and charge carrier leakage into the Alq3 layer. It is expected that with a better host matrix and better electron-transporting layer, these emissions could be eliminated.

## ■ CONCLUSION

In summary, we have successfully synthesized a novel stable green octatwistacene with eight linearly fused benzene rings through one concise D−A reaction. The physical properties have been carefully investigated, and the theoretical calculations were constituent with the experimental results. In addition, the as-prepared octatwistacene has also been employed as an active material in OLED devices.

## ■ EXPERIMENTAL SECTION

**General Procedure.** The 2,6-naphthodiyne precursor (**2**)[8] and 9,11-diphenyl-10*H*-cyclopenta[*e*]pyren-10-one (**3**)[9] were synthesized according to the reported references. All solvents were used without further purification.

**Synthesis of 6,9,16,19-Tetraphenyl-1.20,4.5,10.11,14.15-tetrabenzooctatwistacene (1).** TBAF (1.23 mL of 1 M THF solution, 1.23 mmol) was added dropwise to the solution of 9,11-diphenyl-10*H*-cyclopenta[*e*]pyren-10-one (**3**) (500 mg, 1.23 mmol) and bis(aryne) precursor (**2**) (350 mg, 0.62 mmol) in 60 mL of dry $CH_2Cl_2$. The solution was first stirred at room temperature for 48 h and then was heated to reflux for 24 h. After cooling, the precipitate was collected by filtration, and the pure dark-green solid (**1**) (75 mg, yield of 15%) was obtained after washing with THF. Mp: >300 °C. IR (KBr, cm$^{-1}$) $\nu$: 3052, 1946, 1811, 1442, 1319, 829, 724, 702. $^1$H NMR (THF-$d_8$, 300 MHz) $\delta$: 8.64 (s, 4H), 7.84 (s, 4H), 7.78 (d, 4H, $J$ = 6 Hz), 7.66 (d, 4H, $J$ = 6 Hz), 7.53−7.64 (m, 20H), 7.21 (t, 4H, $J$ = 9 Hz). MS (ESI-TOF) $m/z$: $[M + H]^+$ calcd for $C_{70}H_{41}$ 881.32, found 881.31. Anal. Calcd for $C_{70}H_{40}$: C, 95.42; H, 4.58. Found: C, 95.38; H, 4.62.

**Cyclic Voltammetry (CV) Measurements.** CV was performed in a three-electrode cell solution containing tetrabutylammonium perchlorate/1,2-dichlorobenzene (TBAP/ODCB; recorded at 50 °C) as an electrolyte at a scan rate of 100 mV s$^{-1}$. A Pt wire, glassy carbon, and Ag/AgCl electrode were used as a counter electrode, a working electrode, and a reference electrode, respectively. The potential was externally calibrated against the ferrocene/ferrocenium couple assuming HOMO of Fc/Fc$^+$ to be 4.8 eV.[17]

**Preparation of OLED Devices.** Patterned ITO glasses (15 U/sq) were used as the anode substrates. First, the ITO substrates were cleaned with deionized water, 2-propanol, and acetone in sequence. Subsequently, they were oven-dried and treated in $O_2$ plasma. All thin films and LiF/Al electrodes were fabricated by thermal evaporation in a vacuum deposition system at a pressure of less than $4 \times 10^{-4}$ Pa without breaking the vacuum. All of the organics and metal compounds were evaporated at a rate of about 0.1−0.2 nm s$^{-1}$ (the sublimation temperature for compound **1** is 350 °C), and the metallic electrodes were evaporated at a rate of 0.8−1 nm s$^{-1}$. A shadow mask was used to define the cathode. The luminance current density−voltage (L−J−V) characteristics and electroluminescence (EL) spectra

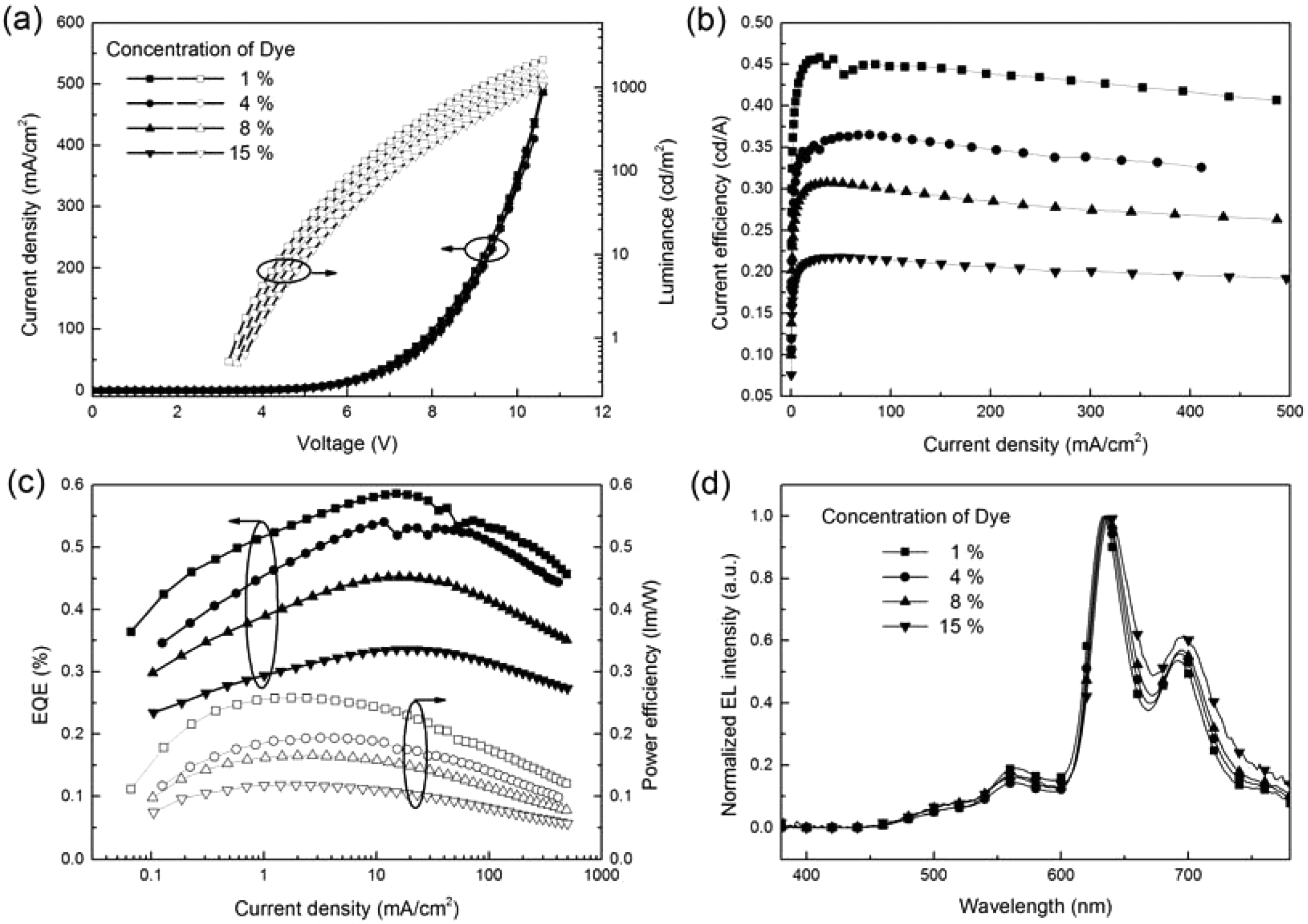

**Figure 6.** (a) Current density−voltage and brightness−voltage spectra of device. (b) Current efficiency versus current density of device. (c) Power efficiency and external quantum efficiency versus current density of device. (d) PL spectra of device with different concentrations of compound **1**.

were measured simultaneously with a Keithley 2400 power source meter and a Photo Research PR 650 spectrometer.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The original TGA, FTIR, $^1$H NMR, and HR-MS spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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