

Soluble and Stable Zethrenebis(dicarboximide) and Its Quinone

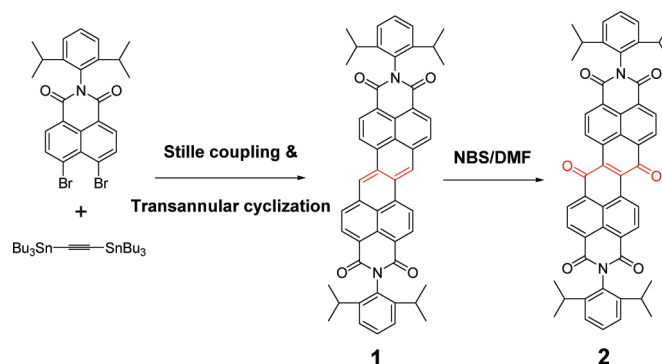
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ABSTRACT



Soluble and stable zethrenebis(dicarboximide) (1) was synthesized by an in situ Stille cross coupling/transannular cyclization reaction. 1 showed largely improved photostability and solubility compared with the very unstable zethrene and it also exhibited far-red absorption and emission with high photoluminescence quantum yield. Bromination of 1 with NBS/DMF gave its quinone form 2 via an unusual pathway.

Zethrene (Figure 1), a hydrocarbon whose synthesis was established 55 years ago, has been forgotten for a long time. The first synthesis of zethrene was achieved by Clar in 1955,¹ and a more convenient access to zethrene was found accidentally by Staab and Sondheimer in the 1960s during their independent attempts to synthesize tetrahydrodinaphtho[10]-annulene, which was highly unstable and could be automatically transformed into zethrene via transannular cyclization.²

It was not until last year that the pure tetrahydrodinaphtho[10]annulene, the precursor to zethrene, was isolated by Tobe's group and they also managed to synthesize stable 7,14-disubstituted zethrene derivatives.³

Zethrene and its derivatives recently attracted increasing interest owing to their potentially interesting properties that might qualify them as new opto-electronic materials for various applications.⁴ Many theoretical predictions have been done to predict the properties of this class of hydrocarbon. In 1995, Burt et al. predicted by PPP calculations that

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zethrenebis(dicarboximide) (e.g., **1** in Scheme 1) would show substantial near-infrared (NIR) absorption and emission,⁵ which is much longer than that of the common rylene diimide dyes.⁶ In 2006, Maksić et al. reported that zethrene as well as its longitudinal homologues would exhibit large absolute proton affinity (APA) and second-order hyperpolarizability (γ) based on semiempirical AM1 calculations, and this was further supported by Nakano's calculations that zethrene will possess a significant singlet diradical character at the ground state (Figure 1). These predictions suggest that zethrene and its derivatives can be used as useful building blocks for nonlinear optical materials and NIR dyes.⁷

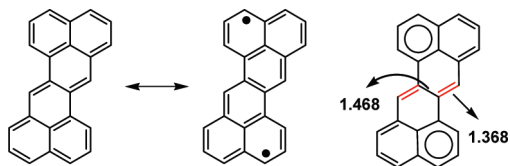
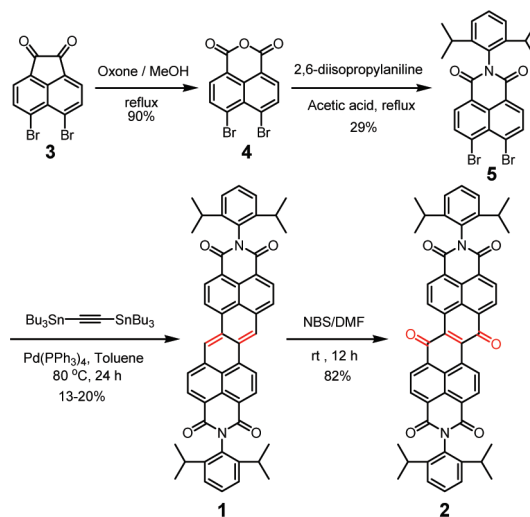


Figure 1. Structural characteristics of zethrene.

Despite all of these attracting properties and promising applications, zethrene and its derivatives were seldom synthesized and studied deeply due to their low accessibility and high sensitivity in the presence of oxygen and light especially in dilute solution.^{3a} Tobe et al. have successfully synthesized 7,14-substituted zethrene by blocking the most reactive 7,14-positions. In parallel to that work, we have been working on the synthesis of electron-withdrawing dicarboxylic imide group substituted zethrene derivative (**1** in Scheme 1). Such an approach will not only stabilize the highly reactive zethrene by lowering its HOMO energy level, but also will result in obvious red-shift of the absorption and emission spectra to the far-red or NIR region owing to the acceptor–donor–acceptor structure. This concept has also been proved to be efficient to prepare soluble and stable NIR dyes by using very unstable hydrocarbons such as bisanthene as building blocks.⁸ In addition, according to calculations, zethrene exhibits a central butadiene moiety flanked by two naphthalene rings and the central butadiene unit shows significant bond length alternation (1.368 and 1.468 Å, Figure 1).⁴ So we can also study the reactivity of the butadiene subunit and perform further modifications at the reactive 7,14-positions. Herein we report an efficient synthesis of a soluble and stable zethrene derivative **1** and its unusual reaction.

Different from previous work, we chose 4,6-dibromo-1,8-naphthalimide (**5**) as precursor with bulky 2,6-diisopropylphenyl as substituent, which can improve the solubility as well as suppress aggregation of the zethrene chromophore. As shown in Scheme 1, 1,8-dibromonaphthoic anhydride (**4**) was first prepared by oxidation of 1,8-dibromoacenaphthenedione (**3**)⁹ with oxone,^{8a} and subsequent imidization of **4** with 2,6-diisopropylaniline afforded 4,6-dibromo-1,8-naphthalimide (**5**).¹⁰ Stille cross coupling reaction¹¹ between **5** and bis(tributylstannyl)acetylene (1:1 ratio) and subsequent in situ transannular cyclization reaction gave the desired zethrenebis(dicarboximide) **1** in one pot. It is essential to carefully control the reaction conditions to obtain the target compound. This reaction must be performed in dilute solution to favor intramolecular cyclization over intermolecular polymerization.¹² Oxygen has to be strictly excluded from the reaction system. The optimized temperature is 80 °C to avoid incomplete conversion at lower temperature or complicated products at higher temperature. Although we did rigid control on the experimental conditions, the separation yield for this step was still low (13–20%) due to the existence of other oligomers, which complicated the column chromatography purification.

Scheme 1. Synthetic Route Toward Compounds **1** and **2**



To further modify the zethrene at the 7,14-positions, bromination of **1** was attempted by using *N*-bromosuccinimide (NBS) in DMF.¹³ Interestingly, the oxidized product zethrenebis(dicarboximide)quinone (**2**) rather than brominated product was formed. The structure of **2** was confirmed by ¹H NMR, ¹³C NMR, HR-ESI MS, MALDI-TOF MS, and

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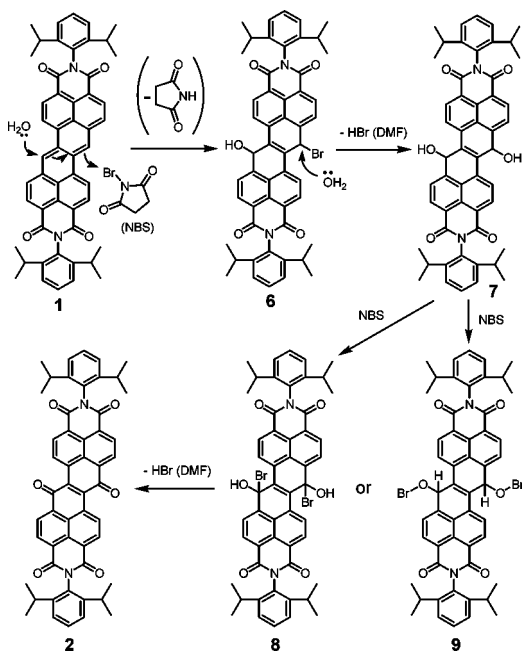
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FT-IR spectra. For example, in the ^{13}C NMR spectrum, two resonances at 186.18 and 163.15 ppm were observed, which can be assigned to carbonyl carbon of the quinone and the imide group, respectively. In the FT-IR spectra of **2**, besides a $\text{C}=\text{O}$ vibration band at 1675 cm^{-1} , which is correlated to the imide unit, an additional $\text{C}=\text{O}$ stretching band at 1715 cm^{-1} related to the quinone structure was also observed (Figure S1, Supporting Information). It is worth noting that no oxidized product but some complicated mixture was obtained if the bromination was conducted in other systems such as NBS/ CHCl_3 and NBS/DMSO. This unusual transformation could be related to the central butadiene character in zethrene.^{1,14} A reasonable mechanism is proposed in Scheme 2. Electrophilic addition of **1** with NBS takes place and subsequent quenching with a trace amount of water in the DMF generates the intermediate **6** with simultaneous formation of succinimide. This is followed by nucleophilic attack of $\text{C}-\text{Br}$ by water to afford the diol **7**. This process is favorable because the Br atom is attached to a benzylic and allylic carbon. In addition, the as-formed HBr molecule can be trapped by the DMF solvent. This also highlights the importance of using basic solvent such as DMF in this conversion. Further bromination of **7** by NBS results in either a substituted intermediate (**8**) or hypobromite intermediate (**9**),¹⁵ both would turn into a zethrene quinone (**2**) after removal of HBr in presence of DMF.

Scheme 2. Proposed Mechanism for the Formation of **2**



Both compounds **1** and **2** are soluble in common organic solvents and **1** exhibits a blue color while **2** appears to be

red. The UV-vis absorption and fluorescence spectra recorded in chloroform are shown in Figure 2. Compound **1** has a major absorption band in the far-red region with a maximum at 648 nm ($\epsilon = 18\,580\text{ M}^{-1}\text{cm}^{-1}$) together with a shoulder at 596 nm. Compared to the maximum absorption of zethrene (550 nm)¹ and 7,14-bis(phenylethynyl)zethrene (576 nm),^{3a} a significant bathochromic shift was observed due to attachment of electron-withdrawing dicarboxylic imide groups, which leads to a convergence of the HOMO-LUMO energy gap.⁵ In contrast to **1**, compound **2** displays a hypsochromic shift with absorption maximum at 477 and 528 nm, indicating that the conjugation of the zethrene core is partially disrupted in the central part. Both **1** and **2** show small Stokes shift due to their rigid backbone. The photoluminescence quantum yield (Φ) of **1** was determined by using Rhodamine B^{16a} and cardiogreen^{16b} as standards and the Φ values were obtained as 0.52 and 0.54, respectively, showing significant enhancement compared with 7,14-bis(phenylethynyl)zethrene ($\Phi = 0.07$).^{3a} Compound **2** exhibits very weak fluorescence due to the existence of the quinone structure. The photostability of **1** in chloroform was also investigated under irradiation of UV light (4 W), white light (100 W), and ambient light, and the half-life times were determined as 35, 600, and 4320 min, respectively (Figures S2–S5, Supporting Information). Such large enhancement on photostability can be explained by the introduction of the electron-withdrawing dicarboxylic imide groups. The quinone **2** showed even higher photostability and the absorption spectra of its solution did not change after standing under ambient conditions for weeks.

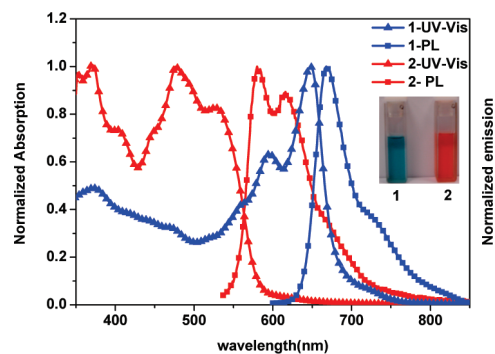


Figure 2. Normalized UV-vis absorption spectra ($5 \times 10^{-5}\text{ M}$) and fluorescence spectra ($5 \times 10^{-5}\text{ M}$) of **1** and **2** in chloroform.

Time-dependent density function theory calculations were conducted for **1** and **2** (see the Supporting Information) and their optimized molecular structures and frontier molecular orbital profiles are shown in Figure 3. For **1**, the carbon-carbon bond lengths of the central part show significant alternation (1.371 and $1.467\text{ \AA}$), indicative of a butadiene-like structure. HOMO of **1** shows electron delocalization through the

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zethrene core to a large extent, and the central two double bonds possess the largest HOMO coefficient, suggesting that the 7,14-positions can easily undergo electrophilic attack, consistent with our observations in the bromination reaction. On the other hand, the LUMO of quinone **2** has a high coefficient along the central quinone unit, thus it has a high tendency to accept electrons. The calculations also predict that compounds **1** and **2** will show absorption maximum at 645.8 and 590.6 nm, which are in agreement with the experimental data.

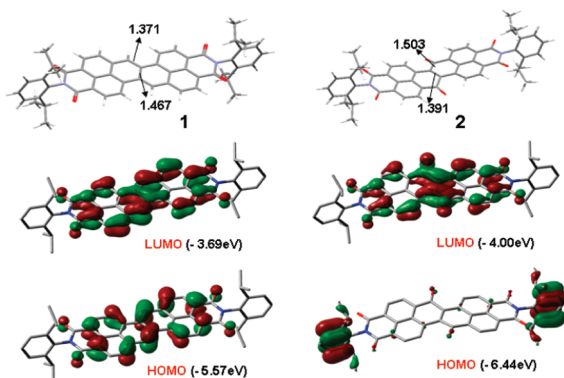


Figure 3. Optimized molecular structures and frontier molecular orbital profiles of **1** and **2**. Some bond lengths are indicated by arrows (Å).

The electrochemical properties of compounds **1** and **2** were investigated by cyclic voltammetry (CV) in dry DCM (Figure 4). The cyclic voltammogram of **1** exhibits one quasi-reversible oxidation wave with half-wave potential (E_{ox}) at 0.93 (vs Fc/Fc⁺) but no obvious oxidation wave was observed for compound **2**. The HOMO energy level of **1** was estimated to be -5.50 eV based on the onset of the oxidation wave.¹⁷ The oxidation potential of **1** is much larger than that of 7,14-bis(phenylethynyl)zethrene (0.29 V in CH₂Cl₂ vs Fc/Fc⁺),^{3a} as well as common semiconductor pentacene (0.3 V vs Fc/Fc⁺ in C₆H₄Cl₂)^{18a} and its bis(triisopropylsilyl)ethynyl derivative (0.38 V vs Fc/Fc⁺ in THF),^{18b} suggesting that a better stability of zethrene derivatives can be achieved by attaching the electron-withdrawing imide group, in accordance with our design at the first place. Compound **1** has shown three reversible reduction waves with half-wave potentials at -0.84 , -0.99 , and -1.30 V, respectively, and there are four reduction potentials for compound **2** at -0.55 , -0.87 , -1.21 , and

-1.67 V. Accordingly, the LUMO energy level of -3.96 eV was calculated for **1** and -4.31 eV for **2** based on the onset of the first reduction wave,¹⁷ indicating that the additional carbonyl groups in **2** increase the electron affinity compared with **1**. It is also worth noting that **1** has a small band gap (1.54 eV), which is in agreement with the optical band gap (1.81 eV) from the absorption spectra.

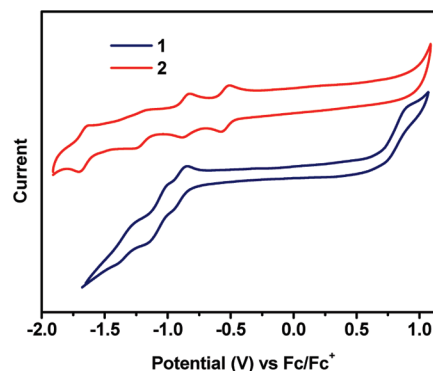


Figure 4. Cyclic voltammograms of compounds **1** and **2** in dichloromethane with 0.1 M Bu₄NPF₆ as supporting electrolyte, Ag/AgCl as reference electrode, Au disk as working electrode, Pt wire as counter electrode, and scan rate at 50 mV/s.

In conclusion, a new zethrene derivative, the zethrenebis(dicarboximide) **1**, was successfully synthesized through an in situ Stille cross coupling/transannular cyclization reaction. Its quinone form **2** was also obtained by chance under typical bromination condition. This unusual chemical transformation can be explained by the existence of a reactive butadiene subunit in compound **1**. Some remarkable chemical and optical properties of **1** were observed such as excellent solubility, good chemical stability and photostability, and high fluorescence quantum yield. Compound **2** shows even better stability and solubility. Preparation of other zethrene derivatives and further investigation of their physical properties are underway in our laboratories.

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Supporting Information Available: Experimental details and characterization data of all new compounds, theoretical calculation data, and photostability test details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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