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7,14-Diaryl-Substituted Zethrene Diimides as Stable Far-Red Dyes with Tunable Photophysical Properties

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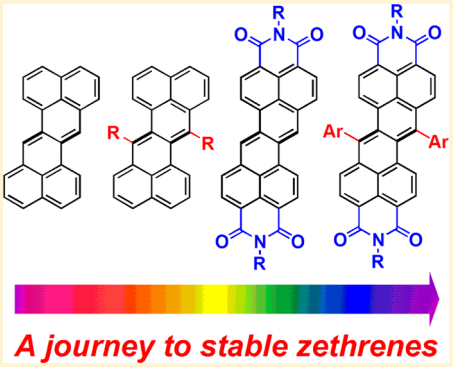
Supporting Information

ABSTRACT: Synthesis and physical characterizations of a series of 7,14-diaryl-substituted zethrene diimides (ZDIs) bearing different substituents (alkyl chain, oligoethyleneglycol ether chain, and aryl group) at the imide sites as well as at the bay regions are described in this study. The synthesis takes advantage of Pd-catalyzed cyclodimerization reaction that allows construction of zethrene core and substitution at the bay region in one single step. The partially cyclized ZDI is also separated as a minor product. The carboxylic acid group is introduced to the bay region for the purpose of further bioconjugation. The photophysical properties, electrochemical properties, and photostability of these ZDI dyes are investigated with UV/vis spectroscopic measurements, cyclic voltammetry measurements, and photoirradiation tests. These dyes exhibit tunable photophysical properties in the far-red spectral region with moderate fluorescent quantum yields and good stability. The enhanced stability as compared to the parent zethrene and the 7,14-substituted zethrenes can be attributed to the electron-withdrawing effect of the imide groups and the kinetic blocking of the most reactive sites at the bay region.



INTRODUCTION

Zethrene refers to a type of *Z*-shaped polycyclic hydrocarbon where two terminal naphthalene units are bridged by one or more butadiene moiety (Figure 1). On the basis of the number of butadiene moieties (n) or the number of six-membered rings (m), the molecule is called zethrene (n = 1, m = 6), heptazethrene (n = 2, m = 7), octazethrene (n = 3, m = 8), and so on. This family of π-conjugated hydrocarbon has long been fascinating to both theoretical chemists and synthetic chemists due to its unique structure and physical properties.[1] Structurally, it represents a rare type of polycyclic hydrocarbon with fixed double bonds in the central part, which makes the central six-membered rings lack aromaticity.[2] Our recent research demonstrated the significant butadiene character of the two bridging double bonds in the smallest member of this family, zethrene, where the two central benzenoid rings undergo electrophilic addition instead of electrophilic substitution.[3] The higher order zethrenes such as heptazethrene and octazethrene are better regarded as a structure where the two naphthalene units are bridged by a *p*-quinodimethane and a 2,6-naphthaquinodimethane, respectively. A large singlet biradical character was theoretically predicted for them due to the recovery of aromaticity of the central benzene and naphthalene moiety upon resonance from a closed-shell quinoidal form to an open-shell biradical form.[4] As a result, these higher order zethrene molecules are highly reactive, which has limited their synthesis for a long time.

The first pursuit of zethrene was reported by Clar in 1955.[5] Since then, a number of synthetic approaches have been developed to access zethrene family, including (a) transannular cyclizations from dehydroannulene species,[6] (b) Pd-catalyzed cyclodimerization,[7] and (c) nucleophilic addition of the corresponding diketone precursor followed by reduction.[8] During the synthesis, thermodynamic stabilization by electron-withdrawing substituents (e.g., dicarboximide) and kinetic stabilization by blocking the most reactive sites are necessary to obtain relatively stable zethrene derivatives. Through these strategies, 7,14-disubstituted zethrenes,[7,9] kinetically blocked heptazethrene and octazethrene,[8] as well as zethrene diimide (ZDI)[3] and heptazethrene diimide (HZ-DI) compounds[10] have been successfully prepared, which allows the experimental examination of many theoretical predictions, such as their large singlet biradical character and their unique third-order nonlinear optical response. Driven by the fast development of the synthetic chemistry of zethrenes, another task seems inevitable: how to make use of these molecules for practical applications? Theoretical works have pointed out a number of possibilities for zethrenes as organic ambipolar semiconductors,[11] nonlinear optical materials,[4,12] and near-infrared dyes.[13] However, the study on this area is still in its early stage, and many obstacles need to be overcome, such as low material stability, lack of functionality, and low scalability. Among all possible applications of zethrenes, one promising direction is to use it as a fluorescent dye in biological systems. Fluorophores based on polycyclic aromatic hydrocarbon (PAH) usually enjoy

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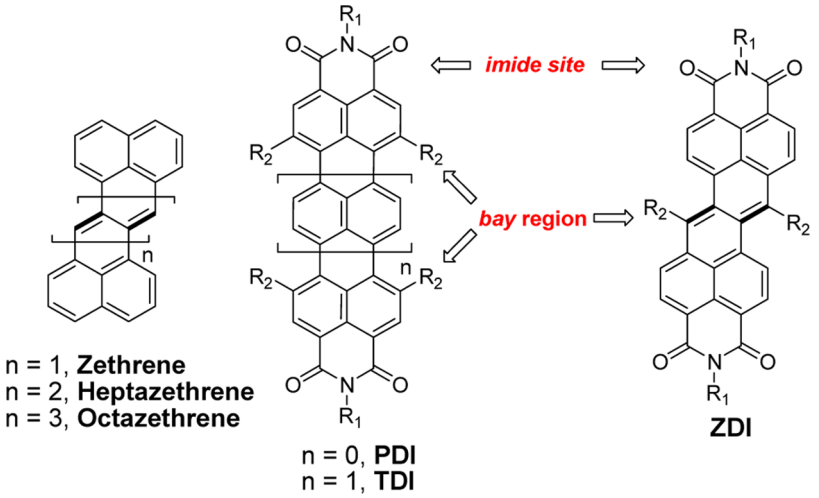
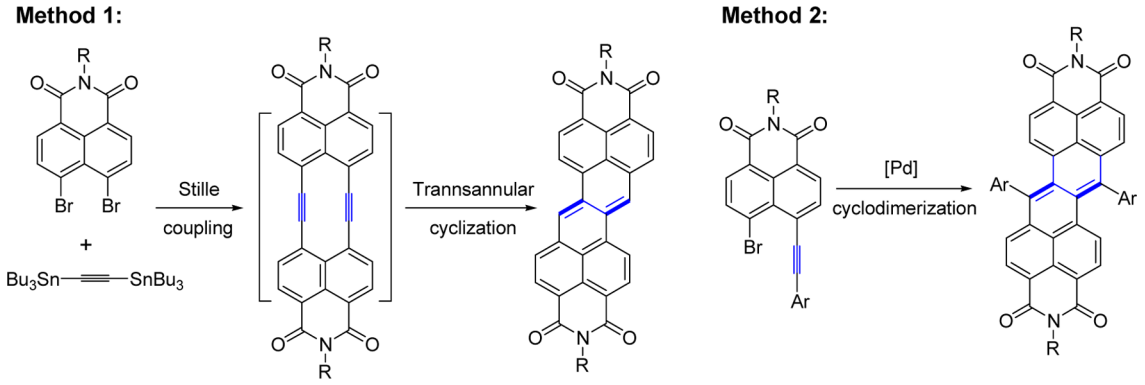


Figure 1. Structures of zethrenes, perylene diimide (PDI), terrylene diimide (TDI), and zethrene diimide (ZDI).

Scheme 1. Two Synthetic Methods of ZDIs



better photostability as compared to commercially available fluorescent dyes (e.g., cyanine dyes),[14] and their performance in biological systems can be optimized once the following criteria are met: (a) water solubility, (b) high photo/chemical stability, (c) high fluorescence intensities, (d) absorption and emission maxima above 600 nm to minimize self-absorption of the biomolecules, (e) the presence of functional groups for attachment onto the biomolecules, and (f) scalable synthesis.[15] One representative example of PAH-based fluorescent dye is the rylene compound.[16] Currently, many works have been dedicated to perylene diimide (PDI) dyes, and a few water-soluble PDIs have been prepared by attaching hydrophilic groups[17] or charged groups[18] onto either the imide sites or the bay regions (Figure 1). The photophysical properties of these dyes have been systematically studied,[19] and they have been successfully employed in the field of bioimaging and biolabeling.[20] However, the absorption spectral region of PDI dyes still falls below 600 nm, and up to now, only few terrylene diimide (TDI) dyes can absorb and emit above 600 nm while maintaining significant fluorescence.[21] On the other hand, zethrene diimide dyes reported by us[3] provide an alternative choice due to the structural similarity to rylene diimides, with both the imide sites and the bay region available for chemical modifications (Figure 1). In addition, ZDIs generally display emission spectra above 650 nm (far-red region) with moderate fluorescence quantum yield,[3] which is desirable for biorelated applications. However, the challenges lie in the stability, the water solubility, the attachment of functional groups, and, above all, the suitable synthetic method.

In the course of seeking stable and soluble ZDI dyes, we previously reported their synthesis by transannular cyclization reactions via a tetradehydro[10]annulene intermediate (method 1, Scheme 1). Unfortunately, this method does not allow further substitution on the bay region as the attempted bromination on the 7,14-positions ends up with oxidized diketone product due to the butadiene character of the central bridge.[3] The stability of the obtained ZDI is not sufficient for practical applications. To further improve the chemical and photostability and to introduce functionality, we expect that the 7,14-diaryl-substituted zethrene diimide should be much more stable due to the attachment of electron-withdrawing imide groups and the kinetic blocking of the most reactive 7,14-positions with high HOMO coefficient. The synthesis can be fulfilled by using the Pd-catalyzed cyclodimerization approach[6] (method 2, Scheme 1), which allows construction of ZDI core and substitution at the bay region in one step. Therefore, a series of **ZDI2**−**ZDI4** with different substituents in the imide sites are prepared, which show tunable photophyscial properties and a large enhancement in stability as compared to **ZDI1** (Figure 2). The different substituents were chosen to serve different purposes; for example, the oligoethyleneglycol ether chains can increase the solubility in polar solvent, while the 2,6-diisopropylphenyl groups are known to be effective for suppressing dye aggregation, thus preventing fluorescence quenching. Moreover, carboxylic acid groups are attached at

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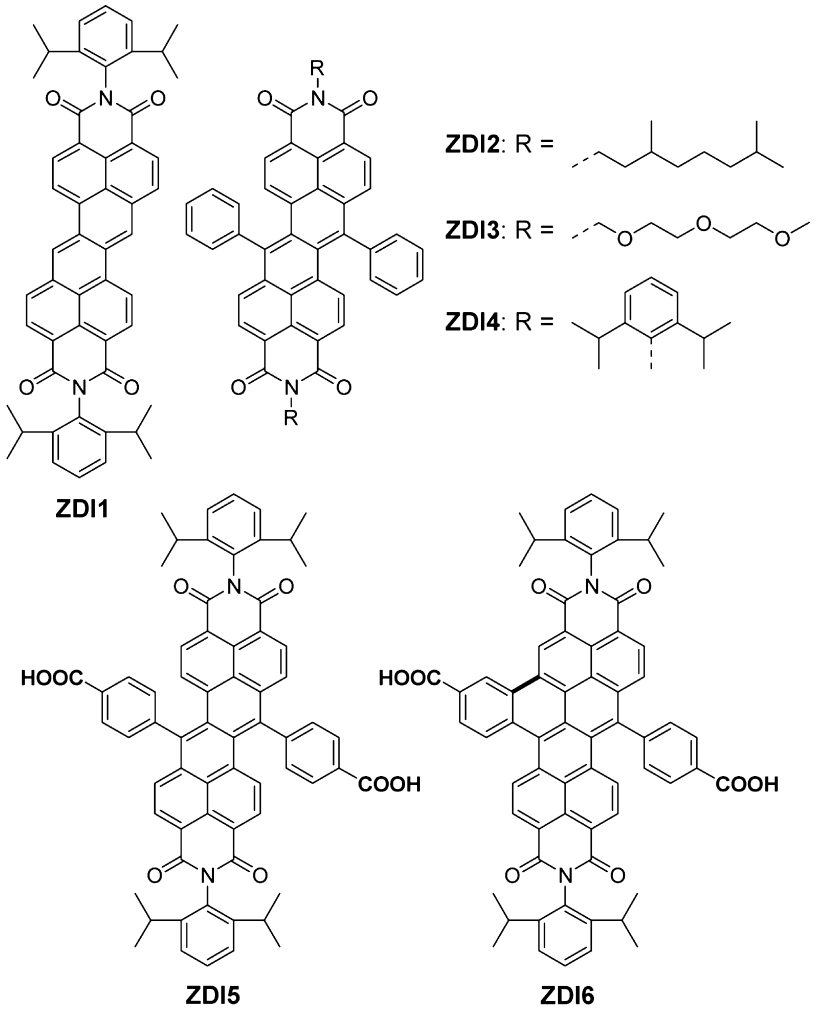

Figure 2. Structures of ZDI derivatives **ZDI1**−**ZDI6**.

the bay region to afford **ZDI5** for the purpose of further conjugation with biomolecules. The partially cyclized **ZDI6** is also obtained as a minor product (Figure 2). Herein, the synthesis, structure, photophysical properties, electrochemical properties, and photostability test of these novel 7,14-diaryl-substituted ZDI far-red dyes are investigated in detail.

RESULTS AND DISCUSSION

Synthesis. The synthesis of all target compounds is outlined in Scheme 2, starting from 1,8-dibromonaphthoic anhydride **2** previously reported by us.[3] Imidization of **2** with 3,7-dimethyloctan-1-amine and 2-(2-(2-methoxyethoxy)ethoxy)-ethanamine in toluene/ethanol mixed solvent under reflux afforded **3** in 80% yield and **4** in 65% yield, respectively. Compound **5** was obtained by reacting **2** with 2,6-diisopropylaniline in refluxing acetic acid. The obtained monoimide intermediates **3**−**5** were then subjected to 1-fold Sonogashira coupling reaction by treating with 1 equiv of phenylacetylene in THF/triethylamine mixed solvents in the presence of $Pd(PPh)_2Cl_2$/CuI. The reaction carried on smoothly at room temperature and gave the monosubstituted products **6**−**8** in 62−70% yield. However, the reaction time must be strictly controlled within 30 min because the 2-fold coupling byproducts will make the separation extremely difficult, especially for compound **7** with oligoethyleneglycol ether substituents. Although the 2-fold coupling byproducts for **7** and **8** cannot be excluded completely, the crude material can be used for the next step directly. Precursors **6**−**8** then were heated to 130 °C in degassed *o*-xylene using $Pd(OAc)_2$/$P(furyl)_3$ as catalyst and Ag_2CO_3 as base to provide the desired **ZDI2**−**ZDI4** as blue solids in 30−35% yield.[22] The structures of **ZDI2**−**ZDI4** were identified by NMR spectroscopy and high-resolution mass spectrometry (Supporting Information).

Efforts were also made to attach carboxylic acid groups at the bay region as functional sites for future bioconjugation. The 2,6-diisopropylphenyl group was chosen as the substituent at the imide site to suppress dye aggregation. As shown in Scheme 2, compound **5** was treated with *tert*-butyl-4-ethynylbenzoate under Sonogashira coupling condition to afford precursor **9** in 75% yield, which was further subjected to similar cyclodimerization condition to give **10** in 28% yield. A partially cyclized product **11** was also isolated as a minor product in 5% yield by silica gel column chromatography, whose polarity was slightly lower than that of **10**. Similar partially cyclized products were also obtained in the cases of **ZDI2** and **ZDI4**, but the amount was quite small. However, in the case of **ZDI3**, no such byproduct was observed. The NMR spectrum of **11** is quite complicated due to the loss in symmetry; however, the structure can be determined with the help of 2D-COSY NMR spectrum and high-resolution mass spectrometry (see the Supporting Information). Hydrolysis of the ester groups in **10**

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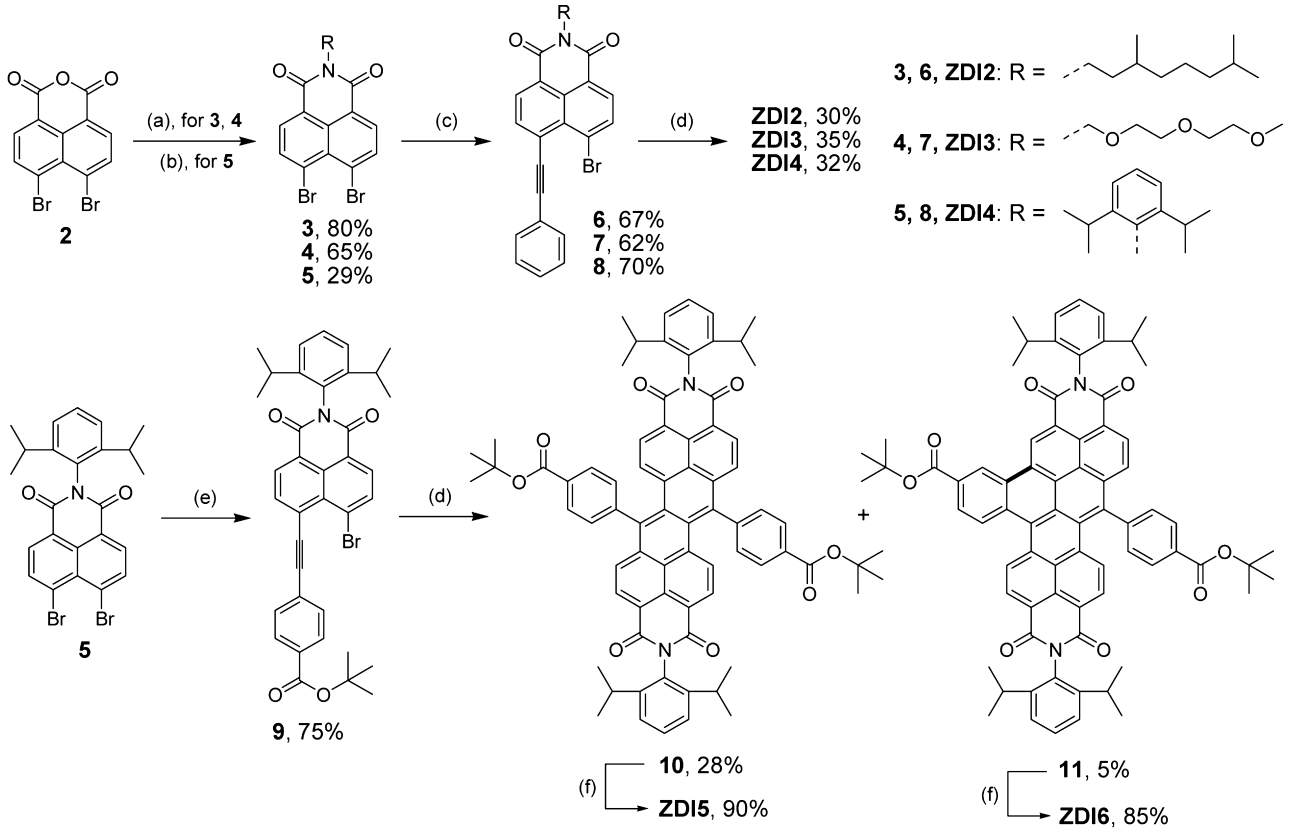
Scheme 2. Synthesis of ZDI2−ZDI6[a]



[a]Synthetic conditions: (a) 3,7-dimethyloctan-1-amine or 2-(2-(2-methoxyethoxy)ethoxy)ethanamine, toluene/ethanol, reflux, 3 h; (b) 2,6-diisopropylaniline, AcOH, reflux, 24 h; (c) phenylacetylene, $Pd(PPh_3)_2Cl_2$, CuI, THF/triethylamine, rt, 30 min; (d) $Pd(OAc)_2$, P(2-furyl)$_3$, Ag_2CO_3, *o*-xylene, 130 °C, 18 h; (e) *t*-butyl-4-ethynylbenzoate, $Pd(PPh_3)_2Cl_2$, CuI, THF/triethylamine, rt, 30 min; (f) trifluoroacetic acid, DCM, rt, 12 h.

and **11** with trifluoroacetic acid (TFA) gave the corresponding acids **ZDI5** and **ZDI6** in 85−90% yield.

Photophysical Properties. All of the obtained ZDI dyes are soluble in common organic solvents including dichloromethane (DCM), $CHCl_3$, and tetrahydrofuran (THF) to give a blue solution, and the solubility is found substituent-dependent in certain solvents. For example, **ZDI1**, **ZDI2**, and **ZDI4** are soluble in hexane but not soluble in polar solvents such as methanol, whereas **ZDI3** and **ZDI5** are soluble in methanol, DMSO, and partially in water due to the presence of hydrophilic groups such as oligoethyleneglycol ether and carboxylic acid units. The UV/vis absorption and fluorescence spectra of **ZDI1−ZDI6**, recorded in DCM, are shown in Figure 3, and the data are collected in Table 1. All ZDI dyes display well-resolved absorption spectra with maxima ranging from 600 to 650 nm, and molar extinction coefficient (ε) on the order of 10^4 M^{-1} cm^{-1}. The absorption wavelength is longer than PDI dyes and is comparable to TDI dyes, which is suitable for bioimaging and biolabeling applications. As compared to **ZDI1**, all 7,14-disubstituted ZDI dyes exhibit 18−41 nm hypsochromic shifts, presumably due to the deviation from planarity induced by the bay-region substitution. In addition, as compared to **ZDI5**, the partially cyclized **ZDI6** displays a hypsochromic shift in absorption, which could be explained by Clar's aromatic sextet rule as **ZDI6** possesses one more aromatic sextet ring in the backbone than **ZDI5**, and similar examples are also reported for other PAHs.[23] On the other hand, all ZDI dyes are fluorescent in DCM with emission maxima ranging from 626 to 704 nm, which is also a desirable window for many biorelated applications. The photoluminescence quantum yield (Φ) was determined according to an optical dilute method (optical density $A < 0.05$) using Rhodamine B as a standard.[24] The 7,14-diaryl-substituted ZDI dyes show moderate quantum yields that are smaller than that of **ZDI1** due to the twisted structure. Moreover, a substituent-dependent phenomenon was also observed. ZDIs with alkyl chains (**ZDI2**) or oligoethyleneglycol ether chains (**ZDI3**) in the imide sites show significantly lower Φ values than **ZDI4** with 2,6-diisopropylphenyl group, which is known to be effective to suppress dye aggregation. The formation of dye aggregation is also evidenced by the concentration-dependent fluorescence measurements (Supporting Information); **ZDI2−ZDI4** exhibit a decrease in the fluorescence intensities with the decrease in solution concentration from 10^{-5} to 10^{-4} M, together with a hypsochromic shift in the fluorescence maxima. This observation suggests that the major fluorescence quenching pathway in this series of dyes is aggregation. It is also worth noting that all 7,14-diaryl-substituted ZDI dyes exhibit larger Stokes shift (ranging from 60 to 74 nm), as compared to **ZDI1** (20 nm), arising from the decrease in rigidity of the structure. A large Stokes shift is one of the crucial requirements for applications in bioimaging.

Electrochemical Properties. The electrochemical properties of **ZDI2−ZDI6** were investigated by cyclic voltammetry (Figure 4) and differential pulse voltommetry (see the Supporting Information) measurements, with anodic scan performed in anhydrous DCM and cathodic sweeping in anhydrous THF. The electrochemical data, including half-wave

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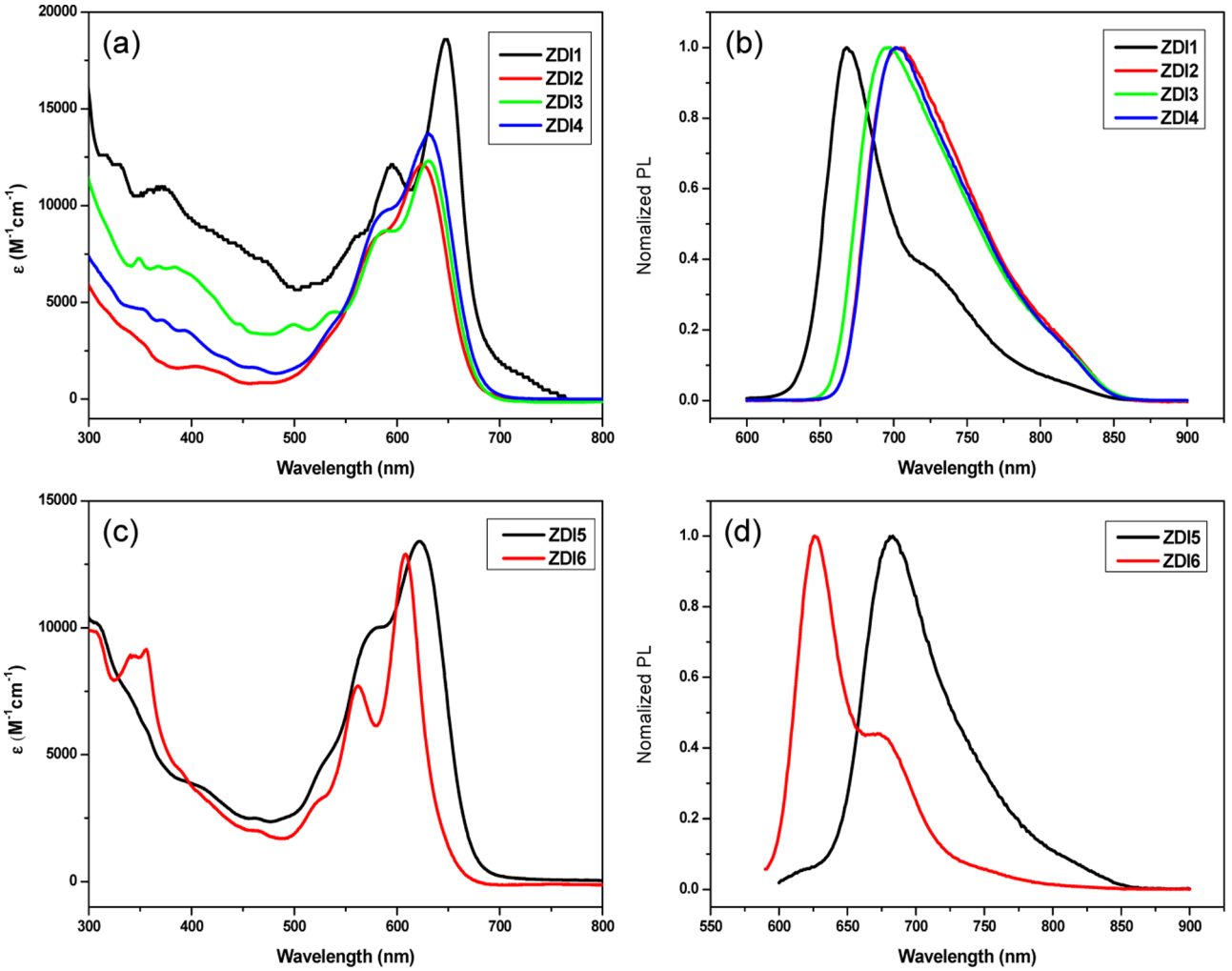

Figure 3. UV−vis absorption and fluorescence spectra recorded in DCM solutions: (a) absorption spectra of **ZDI1**−**ZDI4**, (b) normalized fluorescence spectra of **ZDI1**−**ZDI4**, (c) absorption spectra of **ZDI5** and **ZDI6**, and (d) normalized fluorescence spectra of **ZDI5** and **ZDI6**. The excitation wavelengths for the fluorescence measurements are 590 nm for **ZDI1**−**ZDI5** and 580 nm for **ZDI6**.

Table 1. Photophysical Data of ZDI Compounds ZDI1−ZDI6 Recorded in DCM

compd	λ_{abs} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm)	Stokes shift (cm^{-1})	Φ
ZDI1	648, 596	18 600	668	462	0.53
ZDI2	630, 585	12 100	704	1669	0.13
ZDI3	630, 585	12 300	695	1485	0.05
ZDI4	631, 581	13 700	702	1603	0.24
ZDI5	622, 575	13 400	682	1414	0.30
ZDI6	607, 562	12 900	626	500	0.75

potentials, HOMO, LUMO energy levels, and energy gaps, are listed in Table 2. Electrochemical data for **ZDI1** collected in DCM are also listed for comparison. In general, **ZDI1**−**ZDI4** exhibited one or two quasi-reversible oxidation waves and two to three reversible reduction waves, suggesting that all of these compounds can be reversibly reduced into corresponding anionic species, which can be stabilized by the electron-withdrawing imide groups. The lowest half-wave oxidation potentials fluctuated from 0.84 to 0.93 V (vs Fc/Fc^{+}), showing an anodic shift as compared to the 7,14-disubstituted zethrenes without imide groups (e.g., 0.29 V for 7,14-bis(phenylethynyl)-zethrene) due to the attachment of electron-withdrawing imide groups. For **ZDI5** and **ZDI6**, only irreversible oxidation waves were observed due to the introduction of additional electron-withdrawing carboxylic acid groups in the bay regions, which could further destabilize the cationic species. In both cases, two reversible reduction waves were observed. The HOMO and LUMO energy levels were deduced from the onset potentials of the first oxidation (E_{ox}^{onset}) and the first reduction wave (E_{red}^{onset}), on the basis of the following equations: HOMO = $-(4.8 + E_{ox}^{onset})$ and LUMO = $-(4.8 + E_{red}^{onset})$.[26] The HOMO energy levels of all ZDI dyes range from −5.50 to −5.63 eV, which are quite low lying and suggest a good oxidation resistance. Among them, the HOMO energy levels of 7,14-diaryl-substituted ZDI dyes are slightly lower than that of **ZDI1**, indicating that substitution at the bay regions increases the chemical stability of ZDI dyes. On the other hand, the LUMO energy levels of all ZDI dyes range from −3.87 to −4.05 eV, in which **ZDI5** exhibited the lowest LUMO energy level (−4.05 eV), arising from a high electron affinity that resulted from the synergistic electron-withdrawing effect of imide substitution and the acid substitution. The HOMO−LUMO energy gaps of these ZDI dyes are determined as 1.49−1.66 eV from electrochemical measurements and 1.81−1.92 eV from optical measurements. As compared to **ZDI5**, **ZDI6**

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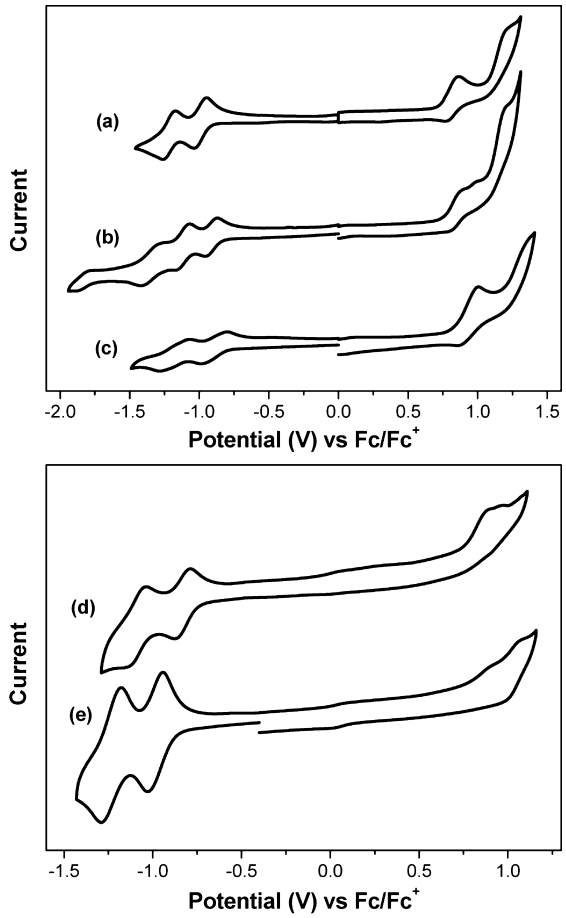

Figure 4. Cyclic voltammograms of (a) **ZDI2**, (b) **ZDI3**, (c) **ZDI4**, (d) **ZDI5**, and (e) **ZDI6** in DCM (for anodic scan) and THF (for cathodic scan) with 0.1 M Bu_4NPF_6 as supporting electrolyte, AgCl/Ag as reference electrode, Au disk as working electrode, Pt wire as counter electrode, and a scan rate of 50 mV s^{-1}.

showed a larger HOMO−LUMO gap, which is in agreement with the blue-shifted absorption maximum.

Photostability Test. The photostability of zethrene derivatives is one of the most essential factors for their preparation, isolation, and application, as zethrene itself is proven to be air- and light-sensitive.[5] Even the 7,14-diphenyl zethrene can be completely decomposed in 12 h upon irradiation with sunlight at room temperature in air.[7] In contrast, all of the ZDI dyes can be stored as solids under ambient conditions for months, despite their smaller band gaps. In solution, the 7,14-diaryl-substituted ZDIs exhibited better stability than the unsubstituted **ZDI1**. The photostabilities of **ZDI1**, **ZDI4**, and **ZDI5** were tested by irradiation with a UV lamp (4 W), a white-light bulb (100 W), and ambient light, and the change of optical intensity at the longest absorption band is plotted against the irradiation time as shown in Figure 5. All dyes degraded with half-life times ($t_{1/2}$) less than 1 h under UV irradiation. In the case of white-light irradiation, **ZDI4** and **ZDI5** displayed much larger enhancement in stability, as **ZDI1** degraded 50% in optical intensity in 10 h while **ZDI4** and **ZDI5** degraded less than 10% during same period. Under ambient condition, **ZDI4** and **ZDI 5** exhibited a significant improvement as compared to **ZDI1** due to the blocking in bay regions. In particular, **ZDI5** showed degradation with less than 10% over more than 10 days. This remarkable enhancement of photostability can be attributed to the electron-withdrawing effect caused by imide and acid substituents, as well as the kinetic blocking of the 7,14-positions at the bay region.

CONCLUSION

In summary, a series of 7,14-diaryl-substituted ZDI molecules (**ZDI2**−**ZDI5**), together with a partially cyclized ZDI molecule (**ZDI6**), were synthesized through Pd-catalyzed cyclodimerization reaction. This synthetic approach allows the bay-region substitutions for ZDI dyes for the first time. The modifications can be done on both imide structure and bay region. The solubility, optical properties, and electrochemical properties are tunable by introducing different substituents. The obtained ZDI dyes are investigated in their photophysical properties, electrochemical properties, and photostability. The good photostability, moderate fluorescence quantum yield, favorable absorption/emission envelope, and attachment of carboxylic acid as bioconjugation sites make them promising candidates for applications in biological systems. The studies on their applications for bioimaging and biolabeling are currently underway in our laboratories.

EXPERIMENTAL SECTION

General. All reagents were purchased from commercial suppliers and used as received without further purification. Anhydrous DCM was distilled from CaH_2, and anhydrous THF was distilled from sodium. 4,6-Dibromo-1,8-naphthalimide **5** and **1** and 8-dibromonaphthoic anhydride **2** were prepared according to our previous report.[3] 3,7-Dimethyloctan-1-amine, 2-(2-(2-methoxyethoxy)ethoxy)-ethanamine, and *t*-butyl-4-ethynylbenzoate were prepared according to the literature.[26] The ^{1}H NMR and ^{13}C NMR spectra were recorded in a solution of $CDCl_3$ with tetramethylsilane (TMS) as the internal standard. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet. MALDI-TOF mass spectra (MS) were recorded using anthracene-

Table 2. Electrochemical Data of ZDI Compounds ZDI1−ZDI6[a]

compd	E_{ox}^1 [V]	E_{ox}^2 [V]	E_{red}^1 [V]	E_{red}^2 [V]	E_{red}^3 [V]	E_{red}^4 [V]	HOMO[b] [eV]	LUMO[b] [eV]	E_g^{EC} [eV][c]	E_g^{Opt} [eV][d]
ZDI1	0.93		−0.84	−0.99	−1.30		−5.50	−3.96	1.54	1.81
ZDI2	0.84	1.18	−1.02	−1.25			−5.53	−3.87	1.66	1.84
ZDI3	0.85	1.17	−0.96	−1.16	−1.40	−1.88	−5.55	−3.96	1.59	1.84
ZDI4	0.90	1.30	−0.95	−1.21	−1.28		−5.63	−4.01	1.62	1.83
ZDI5			−0.89	−1.14			−5.54	−4.05	1.49	1.85
ZDI6			−0.97	−1.20			−5.54	−3.91	1.63	1.92

[a]The redox potentials are calibrated by Fc/Fc^+. [b]HOMO and LUMO energy levels were deduced from the onset potentials of the first oxidation (E^{onset}_{ox}) and the first reduction wave (E^{onset}_{red}), according to the following equations: HOMO = −(4.8 + E^{onset}_{ox}) and LUMO = −(4.8+ E^{onset}_{red}). [c]E_g^{EC} is the electrochemical band gap deduced from the LUMO−HOMO. [d]E_g^{Opt} is the optical band gap estimated from the lowest energy absorption onset.

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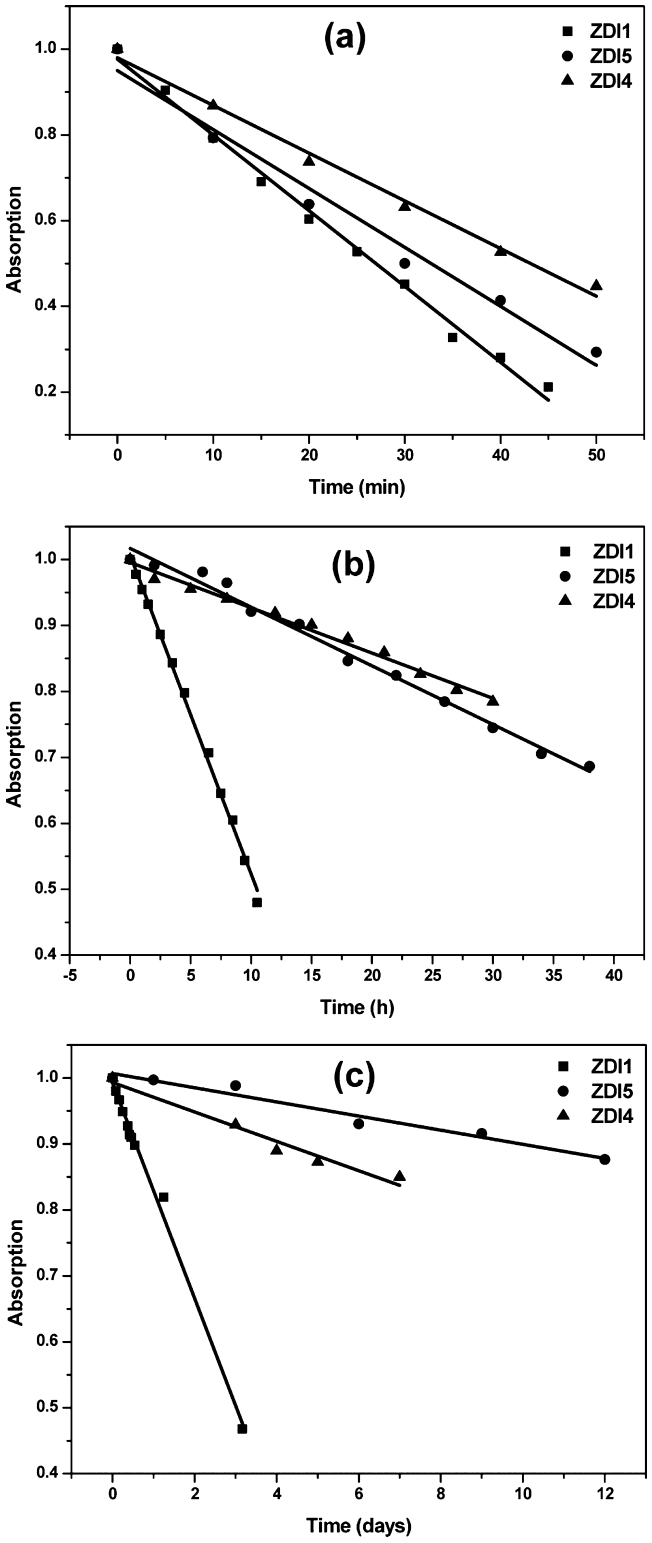

Figure 5. Photostability test of **ZDI1**, **ZDI4**, and **ZDI5** in $CHCl_3$ upon irradiation with (a) UV lamp (254 nm, 4 W), (b) white light bulb (100 W), and (c) ambient light.

1,8,9-triol as matrix. The fluorescence quantum yields were measured by optical dilute method ($A < 0.05$) using Rhodamine B (λ_{abs} = 543 nm, Φ = 0.7 in ethanol) as reference.[25] The electrochemical measurements were carried out in anhydrous DCM and anhydrous THF with 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as the supporting electrolyte at a scan rate of 0.05 V/s at room temperature under the protection of nitrogen. A gold disk was used as working electrode, platinum wire was used as counting electrode, and Ag/AgCl (3 M KCl solution) was used as reference electrode. The potential was calibrated against the ferrocene/ferrocenium couple.

General Synthetic Procedure for 4,6-Dibromo-1,8-naphthalimides. 1,8-Dibromonaphthoic anhydride **2** (1.00 g, 2.83 mmol) was suspended in a mixture solvent of ethanol (20 mL) and toluene (20 mL). To the suspension was added the corresponding amine (5.66 mmol, 2 equiv), and the resulting mixture was then stirred at reflux for 3 h under argon atmosphere. The solvent was then removed, and the residue was purified by column chromatography.

Compound ***3***. 3,7-Dimethyloctan-1-amine was used, and **3** was obtained by column chromatography (silica gel, DCM:hexane = 1:3 (v/v)) as a white solid (1.12 g) in 80% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.32 (d, J = 7.9 Hz, 2H), 8.13 (d, J = 7.9 Hz, 2H), 4.13 (m, 2H), 0.83−1.67 (m, 19H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 162.9, 136.0, 131.3, 131.0, 128.0, 127.5, 123.0, 39.2, 39.1, 37.0, 34.8, 31.2, 27.9, 24.6, 22.7, 22.6, 19.5 ppm. HR−MS (EI): m/z $[M]^+$, calcd for $C_{22}H_{25}O_2NBr_2$, 493.0252; found, 493.0242.

Compound ***4***. 2-(2-(2-Methoxyethoxy)ethoxy)ethanamine was used, and **4** was obtained by column chromatography (silica gel, ethyl acetate:hexane = 1:2 (v/v)) as an orange solid (915 mg) in 65% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.37 (d, J = 3.4 Hz, 2H), 8.18 (d, J = 3.4 Hz, 2H), 4.39 (d, J = 1.9 Hz, 2H), 3.43−3.82 (m, 10H), 3.31 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 163.1, 136.1, 131.5, 128.1, 123.0, 71.8, 70.6, 70.5, 70.1, 67.7, 59.0, 39.4 ppm. HR−MS (EI): m/z $[M]^+$, calcd for $C_{19}H_{19}Br_2NO_5$, 498.9630; found, 498.9627.

General Synthetic Procedure for 4-Bromo-5-arylsilylethynyl-1,8-naphthalimides. 4,6-Dibromo-1,8-naphthalimide (1.00 mmol), $Pd(PPh_3)_2Cl_2$ (0.05 mmol, 5%), and CuI (0.10 mmol, 10%) were dissolved in THF (5 mL) and triethylamine (5 mL) under argon atmosphere. Aryl acetylene (1.20 mmol, 1.2 equiv) was added, and the mixture was stirred at room temperature for 30 min. The mixture was then poured into water and extracted with chloroform. The organic layer was washed with water and brine, each three times, and dried over anhydrous Na_2SO_4. The solvent was removed, and the residue was purified by column chromatography to afford the corresponding product.

Compound ***6***. Compound **3** and phenyl acetylene were used as starting materials, and compound **6** was obtained as a yellow solid (345 mg) in 67% yield by column chromatography (silica gel, DCM:hexane = 1:3 (v/v)). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.53 (d, J = 7.7 Hz, 1H), 8.36 (d, J = 8.1 Hz, 1H), 8.08 (d, J = 7.8 Hz, 1H), 8.04 (d, J = 8.2 Hz, 1H), 7.61 (m, 2H), 7.41 (m, 3H), 4.15 (m, 2H), 0.84−1.73 (m, 19H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 163.3, 163.1, 135.6, 134.6, 131.2, 130.6, 130.0, 129.3, 129.0, 128.6, 127.8, 123.0, 122.6, 103.2, 89.4, 39.3, 39.1, 37.1, 34.9, 31.3, 27.9, 24.6, 22.7, 22.6, 19.5 ppm. HR−MS (EI): m/z $[M]^+$, calcd for $C_{30}H_{30}O_2NBr$, 515.1460; found, 515.1458

Compound ***7***. Compound **4** and phenyl acetylene were used as starting materials, and compound **7** was obtained as a yellow solid (323 mg) in 62% yield by column chromatography (silica gel, ethyl acetate:hexane = 1:2 (v/v)). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.54 (d, J = 7.6 Hz, 1H), 8.36 (d, J = 7.6 Hz, 1H), 8.09 (d, J = 7.6 Hz, 1H), 8.05 (d, J = 7.6 Hz, 1H), 7.62 (m, 2H), 7.42 (m, 3H), 4.41 (m, 2H), 3.31−3.83 (m, 10H), 3.31 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 163.4, 163.2, 135.6, 134.6, 131.7, 131.4, 131.2, 131.1, 131.0, 130.1, 129.3, 129.1, 128.8, 128.6, 128.1, 128.0, 123.0, 122.5, 103.3, 89.3, 71.8, 70.6, 70.5, 70.1, 67.7, 59.0, 39.3, 29.7 ppm. HR−MS (EI): m/z $[M]^+$, calcd for $C_{27}H_{24}O_5NBr$, 521.0838; found, 521.0814.

Compound ***8***. Compound **5** and phenyl acetylene were used as starting materials, and compound **8** was obtained as a yellow solid (375 mg) in 70% yield by column chromatography (silica gel, DCM:hexane = 1:3 (v/v)). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.65 (d, J = 7.5 Hz, 1H), 8.48 (d, J = 8.2 Hz, 1H), 8.19 (d, J = 8.2 Hz, 1H), 8.16 (d, J = 7.5 Hz, 1H), 7.67 (m, 2H), 7.49 (t, J = 8.2 Hz, 1H), 7.44 (m, 3H), 7.34 (d, J = 7.7 Hz, 2H), 2.71 (m, 2H), 1.17 (d, J = 5.7 Hz, 12H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 163.5, 163.3, 145.6, 135.7, 134.7, 131.9, 131.3, 131.2, 130.9, 130.4, 129.7, 129.5, 129.4, 129.2, 128.6,

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128.4, 124.1, 123.0, 122.7, 122.6, 103.6, 89.4, 29.2, 23.9 ppm. HR−MS (EI): m/z $[M]^+$, calcd for $C_{32}H_{26}O_2NBr$, 535.1147; found, 535.1143.

Compound ***9***. Compound **5** and *t*-butyl-4-ethynylbenzoate were used as starting materials, and compound **9** was obtained as a yellow solid (476 mg) in 75% yield by column chromatography (silica gel, DCM:hexane = 1:3 (v/v)). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.66 (d, J = 7.6 Hz, 1H), 8.49 (d, J = 7.7 Hz, 1H), 8.19 (d, J = 8.7 Hz, 1H), 8.17 (d, J = 7.6 Hz, 1H), 8.05 (d, J = 8.2 Hz, 2H), 7.70 (d, J = 8.2 Hz, 2H), 7.48 (t, J = 7.6 Hz, 1H), 7.33 (d, J = 7.6 Hz, 2H), 2.7 (m, 2H), 1.69 (s, 9H), 1.16 (dd, ^4J = 1.3 Hz, ^3J = 6.9 Hz, 12H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 165.0, 163.5, 163.3, 145.6, 136.0, 134.9, 132.5, 132.0, 131.2, 130.9, 130.8, 130.3, 129.7, 129.6, 129.5, 129.0, 12.8, 126.9, 124.1, 123.0, 122.7, 102.5, 91.5, 81.6, 29.2, 28.2, 23.9 ppm. HR−MS (EI): m/z $[M]^+$, calcd for $C_{37}H_{34}O_4NBr$, 635.1671; found, 635.1653.

General Synthetic Procedure for 7,14-Diaryl-zethrenebis-(dicarboximide)s. The corresponding 4-bromo-5-arylsilylethynyl-1,8-naphthalimide (0.3 mmol), $Pd(OAc)_2$ (7 mg, 30 μmol), P(2-furyl)$_3$ (10 mg, 45 μmol), and Ag_2CO_3 (83 mg, 0.3 mmol) were dissolved in *o*-xylene (10 mL) and purged with argon for 20 min, and then the mixture was heated to 130 °C and kept at this temperature for 18 h. After being cooled to room temperature, the solvent was removed under reduced pressure, and the residue was subjected to column chromatography and then preparative TLC to afford the corresponding 7,14-diarylzethrenebis(dicarboximide)s.

ZDI2. Compound **6** was used as a starting material, and **ZDI2** was obtained as a blue solid (40 mg) in 30% yield by column chromatography (silica gel, $CHCl_3$). Analytically pure **ZDI2** was obtained by preparative TLC ($CHCl_3$:hexane = 1:1 (v/v)). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.43 (d, J = 7.6 Hz, 1H), 8.09 (d, J = 8.2 Hz, 1H), 7.53 (m, 3H), 7.42 (d, J = 8.2 Hz, 1H), 7.41 (d, J = 8.2 Hz, 1H), 7.30 (m, 2H), 4.17 (m, 2H), 0.85−1.73 (m, 19H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 163.7, 163.5, 140.9, 137.9, 137.8, 136.0, 133.3, 131.2, 131.0, 130.1, 128.8, 127.7, 125.6, 126.3, 122.1, 121.1, 114.1, 39.3, 39.0, 37.1, 35.1, 31.3, 30.0, 28.0, 24.6, 22.7, 22.6, 19.6 ppm. HR−MS (MALDI-TOF): m/z $[M + H]^+$, calcd for $C_{60}H_{61}N_2O_4$, 873.4626; found, 873.4594.

ZDI3. Compound **7** was used as starting material, and **ZDI3** was obtained as a blue solid (46 mg) in 35% yield by column chromatography (silica gel, ethyl acetate:DCM = 1:10 (v/v)). Analytically pure **ZDI3** was obtained by preparative TLC ($CHCl_3$:ethyl acetate = 5:1 (v/v)). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.43 (d, J = 8.2 Hz, 1H), 8.09 (d, J = 8.2 Hz, 1H), 7.53 (d, J = 6.9 Hz, 2H), 7.42 (d, J = 8.2 Hz, 2H), 7.29−7.31 (m, 3H), 4.42 (t, J = 5.7 Hz, 2H), 3.45−3.83 (m, 10H), 3.33 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 163.7, 163.6, 140.9, 138.0, 137.7, 136.1, 133.3, 131.3, 131.0, 130.9, 130.1, 128.8, 127.8, 126.6, 126.3, 121.9, 120.9, 71.9, 70.6, 70.5, 70.1, 68.0, 59.0, 39.1, 31.9, 31.6, 29.7, 29.3, 22.7, 14.1 ppm. HR−MS (EI): m/z $[M]^+$, calcd for $C_{54}H_{48}N_2O_{10}$, 884.3309; found, 884.3303.

ZDI4. Compound **8** was used as starting material, and **ZDI4** was obtained as a blue solid (44 mg) in 32% yield by column chromatography (silica gel, $CHCl_3$). Analytically pure **ZDI2** was obtained by preparative TLC ($CHCl_3$:hexane = 1:1 (v/v)). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.51 (d, J = 7.6 Hz, 2H), 8.16 (d, J = 8.2 Hz, 2H), 7.58 (m, 5H), 7.52 (d, J = 8.2 Hz, 2H), 7.47 (m, 5H), 7.47 (d, J = 7.9 Hz, 1H), 7.39 (m, 4H), 7.32 (d, J = 7.7 Hz, 4H), 2.72 (m, 4H), 1.15 (d, J = 6.9 Hz, 24H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 163.6, 145.6, 138.4, 137.7, 136.4, 131.7, 131.0, 130.8, 130.2, 130.1, 129.5, 129.4, 129.1, 126.6, 124.1, 124.0, 122.0, 29.1, 24.0 ppm. HR−MS (MALDI-TOF): m/z $[M + H]^+$, calcd for $C_{64}H_{53}N_2O_4$, 913.4000; found, 913.3976.

10* and *11. Compound **9** was used as starting material, **10** was separated as a blue solid (47 mg) in 28% yield (silica gel, R_f = 0.32 in $CHCl_3$), and **11** was separated as a blue solid (8 mg) in 5% yield (silica gel, R_f = 0.38 in $CHCl_3$). For compound **10**, ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.50 (d, J = 8.2 Hz, 2H), 8.20 (d, J = 8.2 Hz, 2H), 8.19 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 8.2 Hz, 2H), 7.47 (t, J = 6.3 Hz, 2H), 7.47 (d, J = 8.2 Hz, 4H), 7.37 (d, J = 7.6 Hz, 2H), 7.33 (d, J = 7.6 Hz, 4H), 2.72 (m, 4H), 1.69 (s, 18H), 1.16 (dd, ^4J = 3.5 Hz, ^3J = 6.9 Hz, 24H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 165.0, 163.6, 163.4, 145.6, 142.1, 140.2, 137.9, 135.8, 133.3, 132.6, 131.8, 131.2, 131.1, 130.7, 130.3, 129.7, 129.6, 128.4, 126.8, 126.5, 124.0, 122.3, 121.4, 81.9, 29.1, 28.2, 24.0 ppm. HR−MS (MALDI-TOF): m/z $[M + H]^+$, calcd for $C_{74}H_{69}N_2O_8$, 1113.5048; found, 1113.5097. For **11**, ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 10.44 (s, 1H), 10.03 (s, 1H), 9.08 (d, J = 9.5 Hz, 1H), 8.90 (d, J = 8.2 Hz, 1H), 8.87 (d, J = 8.2 Hz, 1H), 8.63 (d, J = 7.5 Hz, 1H), 8.49 (dd, ^4J = 1.3 Hz, ^3J = 8.9 Hz, 1H), 8.35 (d, J = 8.2 Hz, 2H), 8.30 (d, J = 8.2 Hz, 1H), 8.00 (d, J = 8.1 Hz, 1H), 7.76 (d, J = 8.2 Hz, 1H), 7.50−7.59 (m, 4H), 7.41 (d, J = 7.6 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 2.79−2.88 (m, 4H), 1.75 (s, 9H), 1.73 (s, 9H), 1.20−1.22 (m, 24H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 165.1, 165.0, 164.3, 164.0, 163.7, 145.7, 143.8, 141.3, 136.6, 135.1, 134.9, 131.7, 131.5, 130.9, 130.8, 130.7, 130.6, 130.3, 130.2, 130.1, 129.7, 129.6, 129.3, 129.2, 128.9, 128.8, 128.2, 127.9, 127.0, 126.9, 126.1, 124.7, 124.2, 124.1, 122.2, 122.0, 121.4, 121.2, 82.4, 82.0, 29.7, 28.3, 24.0 ppm. HR−MS (MALDI-TOF): m/z $[M + H]^+$, calcd for $C_{74}H_{67}N_2O_8$, 1111.4892; found, 1111.4841.

Synthesis of ZDI5 and ZDI6. **10** (20 mg, 0.02 mmol) or **11** (10 mg, 0.01 mmol) was dissolved in DCM, and trifluoroacetic acid (1 mL) was added under argon. The resulting blue solution was stirred at room temperature for 12 h. The solvent was then removed, and **ZDI5** was obtained in 90% yield (18 mg) by column chromatography (silica gel, DCM:ethyl acetate = 5:1 (v/v)). For **ZDI6**, the low solubility in common solvent makes the column chromatography very difficult, so crude product was obtained in 85% yield (8 mg) by washing with hexane.

For **ZDI5**, ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.54 (d, J = 8.0 Hz, 1H), 8.33 (d, J = 8.1 Hz, 2H), 8.19 (d, J = 8.0 Hz, 1H), 7.45−7.57 (m, 4H), 7.40 (d, J = 7.9 Hz, 1H), 7.33 (d, J = 7.7 Hz, 2H), 7.37 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 7.7 Hz, 2H), 2.67−2.75 (m, 2H), 1.16 (d, J = 6.5 Hz, 12H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 170.8, 169.4, 145.6, 143.3, 140.0, 137.7, 135.7, 133.4, 131.9, 131.4, 130.6, 130.3, 130.2, 129.6, 128.4, 126.9, 126.6, 124.1, 122.4, 121.5, 67.7, 45.7, 29.2, 24.0, 21.8, 21.4 ppm. HR−MS (MALDI-TOF): m/z $[M + H]^+$, calcd for $C_{66}H_{53}N_2O_8$, 1001.3796; found, 1001.3778. For **ZDI6**, due to its poor solubility, only high-resolution mass spectrum was recorded. HR−MS (MALDI-TOF): m/z $[M + H]^+$, calcd for $C_{66}H_{51}N_2O_8$, 999.3640; found, 999.3606.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Concentration-dependent fluorescence spectra, NMR spectra, HRMS spectra, and differential pulse voltammograms. 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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■ REFERENCES

(1) Reviews for zethrenes: (a) Clar, E. *Polycyclic Hydrocarbons*; Academic Press: New York, 1964; Vols. *I/II*. (b) Harvey, R. G. *Polycyclic Aromatic Hydrocarbons*; Wiley-VCH: Weinheim, 1997. (c) Umeda, R.; Hibi, D.; Miki, K.; Tobe, Y. *Pure Appl. Chem.* **2010**, *82*, 871−878. (d) Sun, Z.; Wu, J. *J. Mater. Chem.* **2012**, *22*, 4151−4160. (e) Sun, Z.; Ye, Q.; Chi, C.; Wu, J. *Chem. Soc. Rev.* **2012**, *41*, 7857−7889. (f) Sun, Z.; Zeng, Z.; Wu, J. *Chem. Asian J.* **2013**, DOI: 10.1002/asia.201300560.

(2) Clar, E. *The Aromatic Sextet*; Wiley: New York, 1972.

(3) Sun, Z.; Huang, K.-W.; Wu, J. *Org. Lett.* **2010**, *12*, 4690−4693.

(4) Nakano, M.; Kishi, R.; Takebe, A.; Nate, M.; Takahashi, H.; Kubo, T.; Kamada, K.; Ohta, K.; Champagne, B.; Botek, E. *Comput. Lett.* **2007**, *3*, 333−338.
(5) Clar, E.; Lang, K. F.; Schulz-Kiesow, H. *Chem. Ber.* **1955**, *88*, 1520−1527.
(6) (a) Mitchell, R. H.; Sondheimer, F. *J. Am. Chem. Soc.* **1968**, *90*, 530−531. (b) Meinwald, J.; Young, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 725−731. (c) Staab, H. A.; Nissen, A.; Ipaktschi, J. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 226. (d) Mitchell, R. H.; Sondheimer, F. *Tetrahedron* **1970**, *26*, 2141−2150. (e) Staab, H. A.; Ipaktschi, J.; Nissen, A. *Chem. Ber.* **1971**, *104*, 1182−1186.
(7) Wu, T. C.; Chen, C. H.; Hibi, D.; Shimizu, A.; Tobe, Y.; Wu, Y. T. *Angew. Chem., Int. Ed.* **2010**, *49*, 7059−7062.
(8) Li, Y.; Heng, W.-K.; Lee, B. S.; Aratani, N.; Zafra, J. L.; Bao, N.; Lee, R.; Sung, Y. M.; Sun, Z.; Huang, K.-W.; Webster, R. D.; López Navarrete, J. T.; Kim, D.-H.; Osuka, A.; Casado, J.; Ding, J.; Wu, J. *J. Am. Chem. Soc.* **2012**, *134*, 14913−14922.
(9) Umeda, R.; Hibi, D.; Miki, K.; Tobe, Y. *Org. Lett.* **2009**, *11*, 4104−4106.
(10) Sun, Z.; Huang, K.-W.; Wu, J. *J. Am. Chem. Soc.* **2011**, *133*, 11896−11899.
(11) Ruiz-Morales, Y. *J. Phys. Chem. A* **2002**, *106*, 11283−11308.
(12) Knežević, A.; Maksić, Z. B. *New J. Chem.* **2006**, *30*, 215−222.
(13) Désilets, D.; Kazmaier, P. M.; Burt, R. A. *Can. J. Chem.* **1995**, *73*, 319−324.
(14) Haugland, R. P. *Handbook of Fluorescent Probes and Research Products*, 9th ed.; Molecular Probes: Eugene, OR, 2002.
(15) Kobayashi, H.; Ogawa, M.; Alford, R.; Choyke, P. L.; Urano, Y. *Chem. Rev.* **2010**, *110*, 2620−2640.
(16) Reviews for rylenes: (a) Weil, T.; Vosch, T.; Hofkens, J.; Peneva, K.; Müllen, K. *Angew. Chem., Int. Ed.* **2010**, *49*, 9068−9093. (b) Herrmann, A.; Müllen, K. *Chem. Lett.* **2006**, *35*, 978−985. (c) Avlasevich, Y.; Li, C.; Müllen, K. *J. Mater. Chem.* **2010**, *20*, 3814−3826.
(17) (a) Alvino, A.; Franceschin, M.; Cefaro, C.; Borioni, S.; Ortaggia, G.; Bianco, A. *Tetrahedron* **2007**, *63*, 7858−7865. (b) Backes, C.; Schmidt, C. D.; Hauke, F.; Böttcher, C.; Hirsch, A. *J. Am. Chem. Soc.* **2009**, *131*, 2172−2184. (c) Heek, T.; AFasting, C.; Rest, C.; Zhang, X.; Würthner, F.; Haag, R. *Chem. Commun.* **2010**, *46*, 1884−1886. (d) Schmidt, C. D.; Lang, N.; Jux, N.; Hirsch, A. *Chem.-Eur. J.* **2011**, *17*, 5289−5299. (e) Boobalan, G.; Imran, P. M.; Nagarajan, S. *J. Electron. Mater.* **2011**, *40*, 2392−2397. (f) Görl, D.; Zhang, X.; Würthner, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 6328−6348.
(18) (a) Rehm, S.; Stepanenko, V. R.; Zhang, X.; Rehm, T. H.; Würthner, F. *Chem.-Eur. J.* **2010**, *16*, 3372−3382. (b) Schönamsgruber, J.; Schade, B.; Kirschbaum, R.; Li, J.; Bauer, W.; Böttcher, C.; Drewello, T.; Hirsch, A. *Eur. J. Org. Chem.* **2012**, 6179−6186. (c) Sun, J.; Wang, M.; Xu, P.; Zhang, S.; Shi, Z. *Synth. Commun.* **2012**, *42*, 1472−1479.
(19) Kohl, C.; Weil, T.; Qu, J.; Müllen, K. *Chem.-Eur. J.* **2004**, *10*, 5297−5310.
(20) (a) Qu, J.; Kohl, C.; Pottek, M.; Müllen, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 1528−1531. (b) Weil, T.; Abdalla, M. A.; Jatzke, C.; Hengstler, J.; Müllen, K. *Biomacromolecules* **2005**, *6*, 68−79. (c) Peneva, K.; Mihov, G.; Herrmann, A.; Zarrabi, N.; Börsch, M.; Duncan, T. M.; Müllen, K. *J. Am. Chem. Soc.* **2008**, *130*, 5398−5399. (d) Gao, B.; Li, H.; Liu, H.; Zhang, L.; Bai, Q.; Ba, X. *Chem. Commun.* **2011**, *47*, 3894−3896. (e) Céspedes-Guirao, F. J.; Ropero, A. B.; Font-Sanchis, E.; Nadal, Á.; Fernández-Lázaro, F.; Sastre-Santos, Á. *Chem. Commun.* **2011**, *47*, 8307−8309. (f) Yang, S. K.; Shi, X.; Park, S.; Doganay, S.; Ha, T.; Zimmerman, S. C. *J. Am. Chem. Soc.* **2011**, *133*, 9964−9967. (g) Wang, L.; Xu, L.; Neoh, K. G.; Kang, E.-T. *J. Mater. Chem.* **2011**, *21*, 6502−6505. (h) Liu, H.; Wang, Y.; Liu, C.; Li, H.; Gao, B.; Zhang, L.; Bo, F.; Baia, Q.; Ba, X. *J. Mater. Chem.* **2012**, *22*, 6176−6181.
(21) (a) Peneva, K.; Mihov, G.; Nolde, F.; Rocha, S.; Hotta, J.; Braeckmans, K.; Hofkens, J.; Uji-i, H.; Herrmann, A.; Müllen, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 3372−3375. (b) Jung, C.; Müller, B. K.; Lamb, D. C.; Nolde, F.; Müllen, K.; Bräuchle, C. *J. Am. Chem. Soc.* **2006**, *128*, 5283−5291.
(22) In Y.-T. Wu's report (ref 7), the reaction yield can be up to 73%. The decreased reaction yield could be attributed to lower reactivity of Br as compared to I. Also in Wu's case, one substrate with Br group did not give the corresponding cyclodimerization product.
(23) Li, J.; Jiao, C.; Huang, K.-W.; Wu, J. *Chem.-Eur. J.* **2011**, *17*, 14672−14680.
(24) López Arbeloa, F.; Ruiz Ojeda, P.; López Arbeloa, I. *J. Lumin.* **1989**, *44*, 105112.
(25) (a) Pommerehne, J.; Vestweber, H.; Guss, W.; Mahrt, R. F.; Bassler, H.; Porsch, M.; Daub, J. *Adv. Mater.* **1995**, *7*, 551−554. (b) Chi, C.; Wegner, G. *Macromol. Rapid Commun.* **2005**, *26*, 1532−1537.
(26) (a) Clerc, J.; Schellenberg, B.; Groll, M.; Bachmann, A. S.; Huber, R.; Dudler, R.; Kaiser, M. *Eur. J. Org. Chem.* **2010**, 3991−4003. (b) Taylor, E. C.; Wong, G. S. K. *J. Org. Chem.* **1989**, *54*, 3618−3624.