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7,14-Diaryl-substituted Zethrene Diimides as Stable Far-red Dyes with Tunable Photophysical Properties

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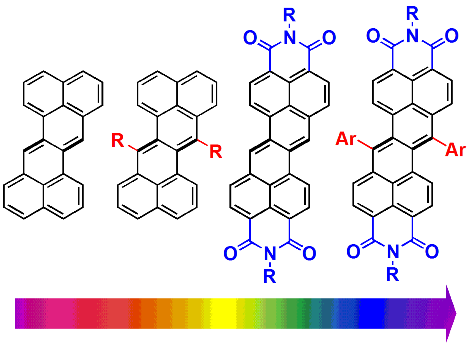
TOC Graphic



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 bio-conjugation. The photo-physical properties, electrochemical properties and photo-stability of these ZDI dyes are investigated with UV/Vis spectroscopic measurements, cyclic voltammetry measurements and photo-irradiation tests. These dyes exhibit tunable photophysical properties in the

far-red spectral region with moderate fluorescent quantum yields and good stability. The enhanced stability 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). Based on the number of the butadiene moieties (n) or the number of the 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 of 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.

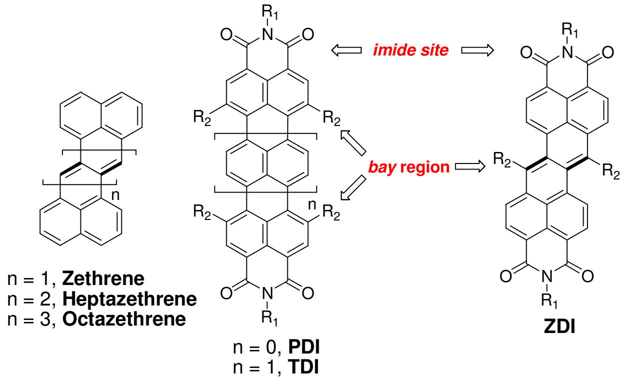
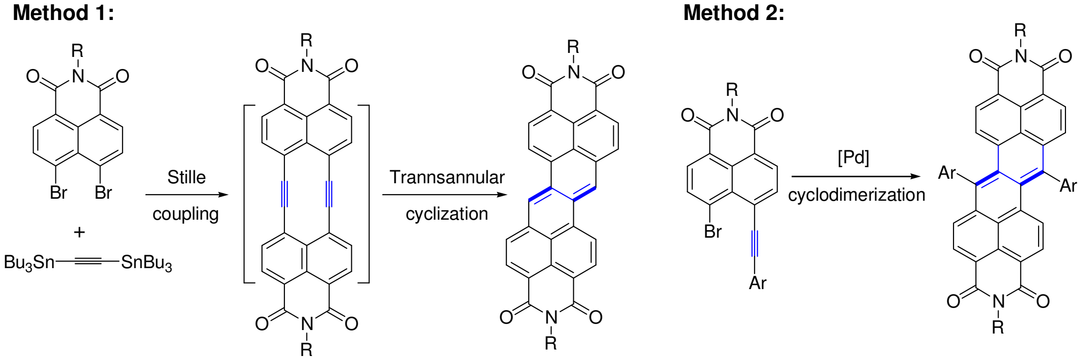


Figure 1. Structures of zethrenes, perylene diimide (PDI), terrylene diimide (TDI) and zethrene diimide (ZDI).

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 non-linear 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 better photo-stability 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 bio-molecules, (e) presence of functional groups for attachment onto the bio-molecules 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 bio-imaging and bio-labeling.[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 maintain 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 bio-related applications. However, the challenges lie in the stability, the water solubility, the attachment of functional groups and above all, the suitable synthetic method.



Scheme 1. Two synthetic methods of ZDIs.

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

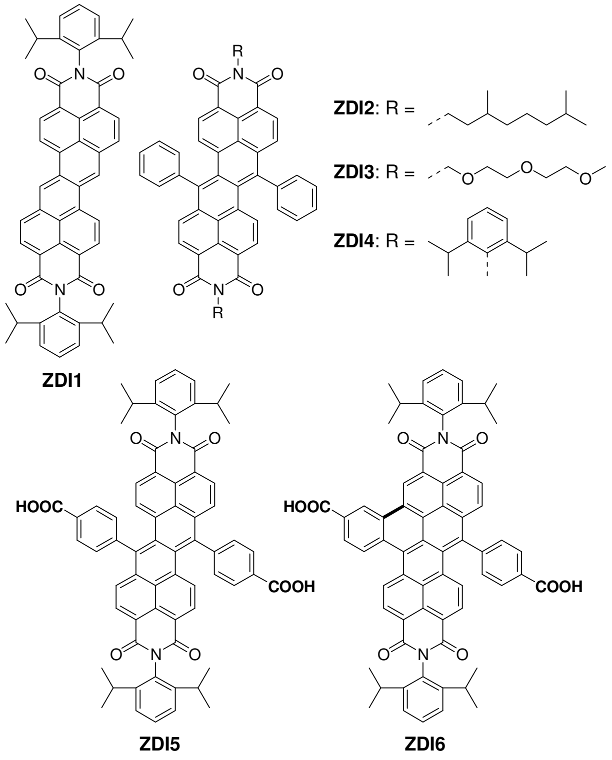
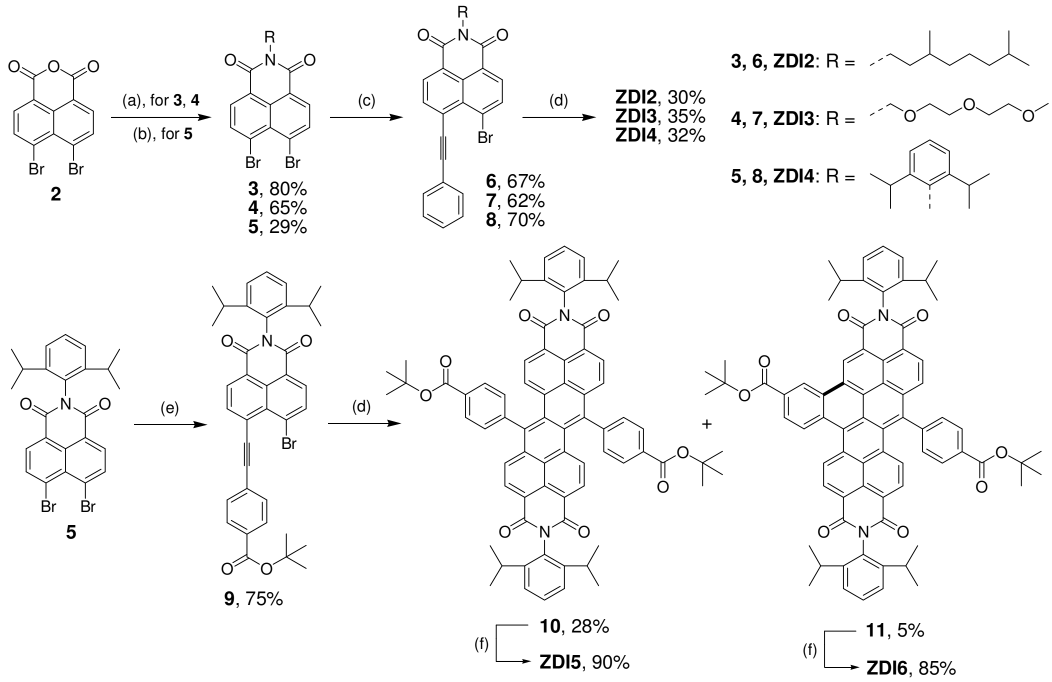


Figure 2. Structures of ZDI derivatives **ZDI1**-**ZDI6**

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 one fold Sonogashira coupling reaction by treating with 1 equivalent phenylacetylene in THF/triethylamine mixed solvents in presence of $Pd(PPh)_2Cl_2$/CuI. The reaction carried on smoothly at room temperature and gave the mono-substituted products **6**-**8** in 62-70% yield. However, the reaction time must be strictly controlled within 30 minutes since the two-fold coupling by-products will make the separation extremely difficult, especially for compound **7** with oligoethyleneglycol ether substituents. Although the two-fold coupling by-products for **7** and **8** cannot be excluded completely, the crude material can be used for the next step directly. Then, the precursors **6-8** were heated up to 130 ^{o}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 (SI)).

The efforts were also made to attach carboxylic acid groups at the bay region as functional sites for future bio-conjugation. 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 **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 by-product 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 SI). Hydrolysis of the ester groups in **10** and **11** with trifluoroacetic acid (TFA) gave the corresponding acids **ZDI5** and **ZDI6** in 85-90% yield.



Scheme 2. Synthesis of **ZDI2**-**ZDI6**. Synthetic conditions: (a) 3,7-dimethyloctan-1-amine or 2-(2-(2-methoxyethoxy)ethoxy)ethanamine, toluene/ethanol, reflux, 3h; (b) 2,6-diisopropylaniline, AcOH, reflux, 24h; (c) phenylacetylene, Pd(PPh$_3$)$_2$Cl$_2$, CuI, THF/triethylamine, RT, 30 mins; (d) Pd(OAc)$_2$, P(2-furyl)$_3$, Ag$_2$CO$_3$, *o*-xylene, 130 °C, 18h; (e) *t*-butyl-4-ethynylbenzoate, Pd(PPh$_3$)$_2$Cl$_2$, CuI, THF/triethylamine, RT, 30 mins; (f) trifluoroacetic acid, DCM, RT, 12h.

Photophysical properties: All 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-dependant 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 nm to 650 nm, and molar extinction coefficient (ε) in 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 bio-imaging and bio-labeling applications. 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, 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 nm to 704 nm, which is also a desirable window for many bio-related applications. The photoluminescence quantum yield (Φ) were 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 and smaller than that of **ZDI1** due to the twisted structure. Moreover, a substituent-dependant 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-dependant fluorescence measurements (SI), **ZDI2-ZDI4** exhibit decrease in the fluorescence intensities with the decrease in solution concentration from 10^{-5} M 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 nm to 74 nm), 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 bio-imaging.

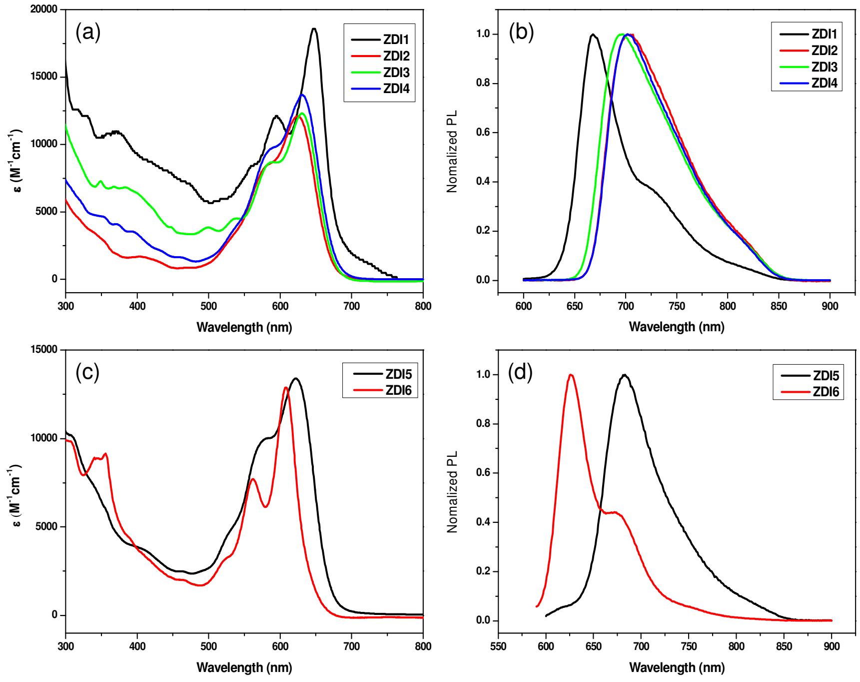


Figure 3. UV-Vis absorption and fluorescence spectra recorded in DCM solutions: (a) absorption spectra of **ZDI1**-**ZDI4**, (b) normalized fluorescence spectra of **ZDI1**-**ZDI4**, (c) absorption spectra of **ZDI5** and **ZDI6**, and (d) normalized fluorescence spectra of **ZDI5** and **ZDI6**. The 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	18600	668	462	0.53
ZDI2	630, 585	12100	704	1669	0.13
ZDI3	630, 585	12300	695	1485	0.05
ZDI4	631, 581	13700	702	1603	0.24
ZDI5	622, 575	13400	682	1414	0.30
ZDI6	607, 562	12900	626	500	0.75

Electrochemical properties: The electrochemical properties of **ZDI2**-**ZDI6** were investigated by cyclic voltammetry (Figure 4) and differential pulse voltommetry (see SI) measurements, with anodic scan performed in anhydrous DCM and cathodic sweeping in anhydrous THF. The electrochemical data, including half-wave potentials, HOMO, LUMO energy levels and energy gaps are listed in Table 2. Electrochemical data for **ZDI1** collected in DCM is 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 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 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 a 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 are ranging from -5.50 eV 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 are ranging from -3.87 eV to -4.05 eV, in which **ZDI5** exhibited the lowest LUMO energy level (-4.05 eV), arising from a high electron affinity resulted from 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 eV to 1.66 eV from electrochemical measurements and 1.81 eV to 1.92 eV from optical measurements. Compared to **ZDI5**, **ZDI6** showed a larger HOMO-LUMO gap which is in agreement with blue shifted absorption maximum.

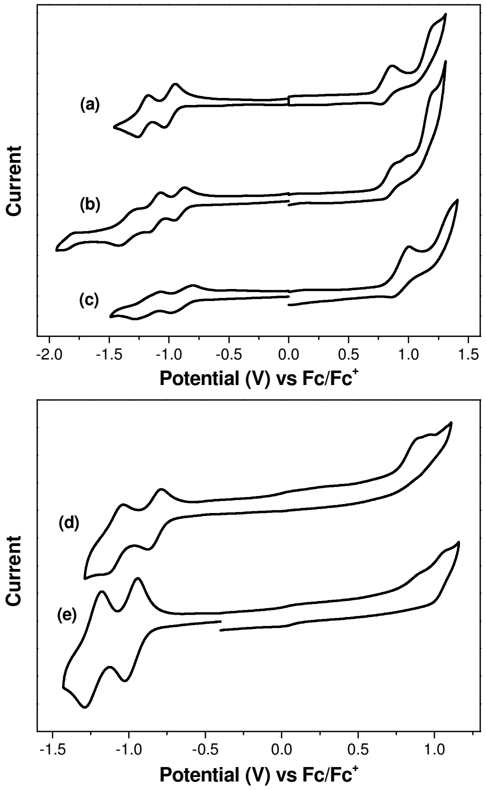


Figure 4. Cyclic voltammograms of (a) **ZDI2**, (b) **ZDI3**, (c) **ZDI4**, (d) **ZDI5** and (e) **ZDI6** in DCM (for anodic scan) and THF (for cathodic scan) with 0.1M Bu_4NPF_6 as supporting electrolyte, AgCl/Ag as reference electrode, Au disk as working electrode, Pt wire as counter electrode, and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

Table 2. Electrochemical data of ZDI compounds **ZDI1**-**ZDI6**.[a]

Compt	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 ($E^{\text{onset}}_{\text{ox}}$) and the first reduction wave ($E^{\text{onset}}_{\text{red}}$), according to the following equations: HOMO = -(4.8+ $E^{\text{onset}}_{\text{ox}}$) and LUMO = -(4.8+ $E^{\text{onset}}_{\text{red}}$). [c] E_g^{EC} is the electrochemical band gap deduced from the LUMO-HOMO. [d] E_g^{Opt} is optical band gap estimated from the lowest energy absorption onset.

Photo-stability test: The photo-stability 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 hours upon irradiation with sunlight at room temperature in air.[7] In contrast, all 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 photo-stability 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 hour 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 hours while **ZDI4** and **ZDI5** degraded less than 10% during same period. Under ambient condition, **ZDI4** and **ZDI 5** exhibited a significant improvement 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 photo-stability 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.

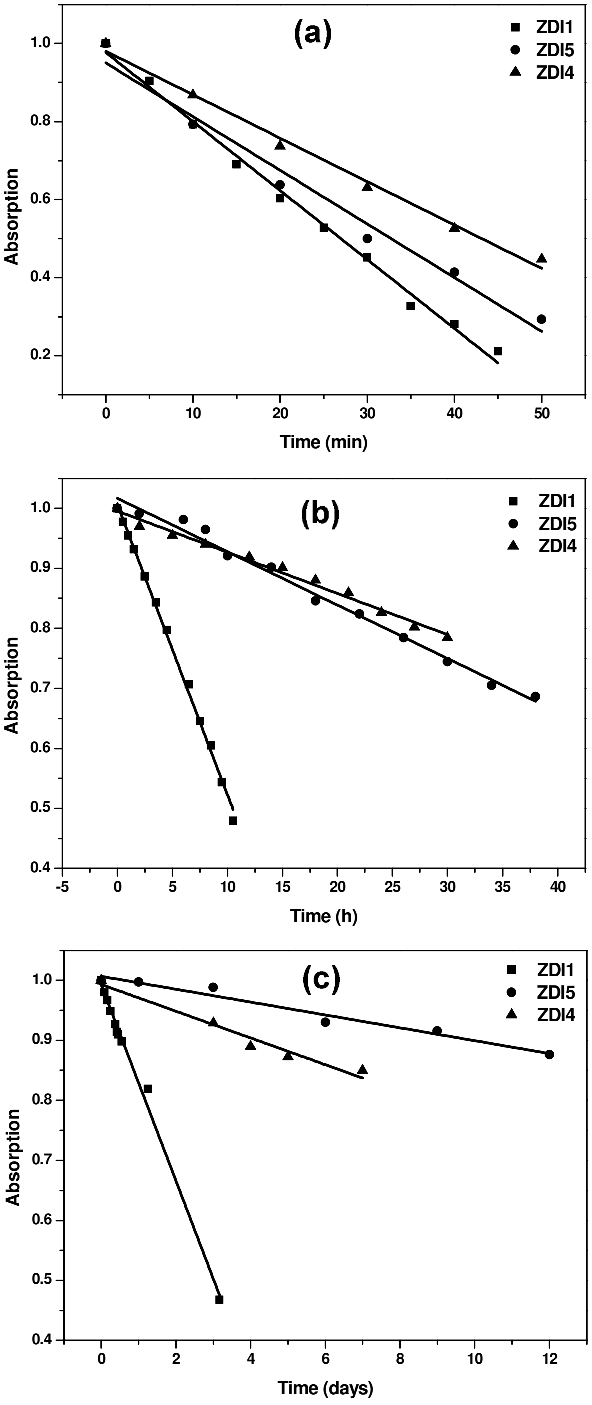


Figure 5. Photo-stability test of **ZDI1**, **ZDI4** and **ZDI5** in $CHCl_3$ upon irradiation with (a) UV lamp (254 nm, 4W), (b) white light bulb (100 W) and (c) ambient light.

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 photo-stability. The good photo-stability, moderate fluorescence quantum yield, favourable absorption/emission envelope and attachment of carboxylic acid as bio-conjugation sites make them promising candidates for applications in biological systems. The studies on their applications for bio-imaging and bio-labeling 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**, 8-dibromonaphthoic anhydride **2** was 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 literature.[26] The ^1H NMR and ^{13}C NMR spectra were recorded in 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-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 0.1M 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 (3M 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 corresponding amine (5.66 mmol, 2 equiv.) and the resulted mixture was then stirred at reflux for 3 hours 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 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 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%), 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 in room temperature for 30 minutes. The mixture was then poured into water and extracted with chloroform. The organic layer was washed with water and brine, each for 3 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, 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 minutes, then the mixture was heated up to 130 °C and kept at this temperature for 18 hours. After 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 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)). ^1H 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**, ^1H 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**, ^1H 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 resulted 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.

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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.

REFERENCES

[1] Reviews for zethrenes: (a) Clar, E. *Polycyclic Hydrocarbons,* Vol. I/II, Academic Press, New York, **1964**; (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, **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.; Fasting, 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. *Synthetic. 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 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.