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# Synthesis and Structure-Linear and Structure-Nonlinear Optical Properties of Multi-Dipolar Zigzag Oligoaryleneethynylenes

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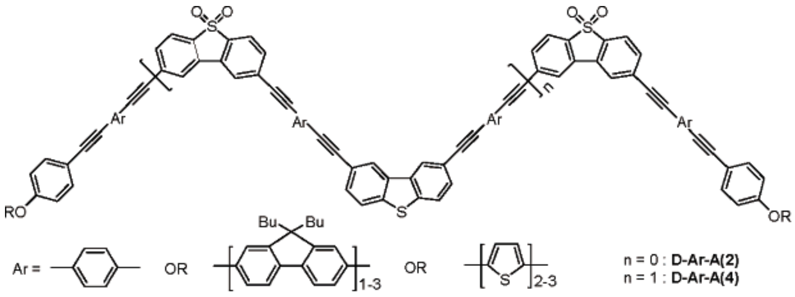

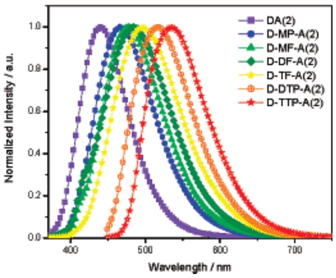

A novel series of monodisperse, multi-dipolar zigzag oligoaryleneethynylenes **DA(*n*)** and **D-Ar-A(*n*)**, bearing electron-donating dibenzothiophene and electron-accepting dibenzothiophene dioxide as arenes, with up to six charge-transfer (dipolar) units have been designed and synthesized by palladium-catalyzed Sonogashira coupling reactions. The linear and nonlinear optical properties of these multi-dipolar oligoaryleneethynylenes can easily be modified or enhanced by incorporating/extending with various central aryleneethynyl moieties such as phenylethynyl, oligo(9,9-dibutylfluorenyl)ethynyl, and oligothienylethynyl within the donor−acceptor units. Interestingly, the absorption and emission of these zigzag oligoaryleneethynylenes are not dependent on the number of covalently linked dipolar chromophores; however, the fluorescence quantum efficiencies consistently decrease with increased number of covalently linked dipolar units. These zigzag oligoaryleneethynylenes exhibit a linear increase in the two-photon absorption (TPA) cross-sections with increased number of covalently linked dipolar units without red-shifting the absorption and emission spectra. In addition, very large TPA cross-sections in the femtosecond regime ($\sigma_{800} = 1306$ GM in DMF or $\sigma_{750} = 1522$ GM in $CH_2Cl_2$) were obtained for **D-TF-A(4)** despite the moderate strength of the donor−acceptor pair. Our results suggest that the TPA properties of these zigzag oligoaryleneethynylenes including TPA wavelength and TPA cross-section can easily be tuned by means of modifying the central aryleneethynylene units and increasing the number of dipolar units, respectively. This approach provides an alternative means to tune or enhance the TPA cross-section at a specific wavelength.

## Introduction

Nonlinear optical materials that exhibit large two-photon absorption (TPA) cross-sections ($\sigma$) have drawn considerable attention recently as they show potential applications in various emerging technologies, which include three-dimensional optical data storage,[1] two-photon optical power limiting,[2] two-photon excited fluorescence (TPEF) microscopy,[3] photodynamic therapy,[4] and two-photon microfabrication.[5] There has been significant progress in designing and synthesizing one-dimensional chromophores such as dipolar and quadrupolar molecules with large TPA cross-sections, which generally increases with the donor/

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acceptor strength, conjugated length, and planarity of the $\pi$-conjugated system.[6] However, such structural modifications often shift the two-photon absorption maximum to a longer wavelength because of the enhanced $\pi$-conjugation/electron delocalization. On the other hand, strategy/guideline that can enhance the TPA cross-section at a specific wavelength, i.e., 800 nm, is rather limited. TPA-active molecules that can exhibit large $\sigma_{800}$ at 800 nm excitation wavelength are particularly important as it is the most accessible and useful laser wavelength for practical applications, i.e., TPEF microscopy. More recently, the introduction of multidimensional $\pi$-conjugated systems, in which the active chromophores extend into two or three dimensions, offers a new opportunity to enhance the nonlinear optical properties in different aspects. This has led to the development of highly TPA-active multibranched chromophores, octupolar molecules, and dendrimers.[7] The TPA enhancement of multidimensional $\pi$-conjugated systems arises either from the increase in the number of chromophore density or from the $\pi-\pi$ interactions among $\pi$-conjugated moieties or chromophores. As a result, studies of multidimensional $\pi$-conjugated chromophoric systems may also provide insight into the influence of chromophoric interaction on the functional properties of a material as the bulk (or material) performance of chromophores depends greatly on the molecular arrangement in the solid state and the morphology of a material.

Oligoaryleneethynylenes, in which arene moieties are connected by the ethynyl bridge, constitute one of the widely investigated $\pi$-conjugated molecules. Substantial work has been done to modulate or enhance a specific functional property of linear oligoaryleneethynylenes[8] such as electrical conductivity, optical nonlinearity, and sensing property by means of applying different types of arene moieties such as benzene, thiophene, anthracene, pyridine, or pyrimidine to the system. The merit of using an ethynyl unit as a conjugated bridge is that it possesses an excellent photochemical stability,[9] which is particularly important for nonlinear optical materials. In contrast to linear oligoaryleneethynylenes, zigzag oligomers are not widely explored for use as a functional material.[10]

We describe herein the synthesis and structure-linear and -nonlinear optical investigation of a novel series of multi-dipolar chromophores, namely multi-dipolar zigzag oligoarylene−ethynylenes, **DA(*n*)** and **D-Ar-A(*n*)**, which exhibit tunable TPA wavelength and TPA cross-sections based on electron-donating dibenzothienylethynyl and electron-accepting dibenzothienylethynyl dioxide as arene units, respectively. We have shown that the linear/nonlinear optical properties of these zigzag oligoaryleneethynylenes can easily be modified by incorporating/extending with various central aryleneethynyl units such as phenylethynyl, oligo(9,9-dibutylfluorenyl)ethynyl, and oligothienylethynyl within the charge transfer (dipolar) units. We have also demonstrated that the TPA cross-sections of these zigzag oligoaryleneethynylenes can be enhanced by the number of dipolar chromophores incorporated without causing the red-shift of the TPA band.

## Results and Discussion

To enhance the solubility of the longer homologues of the zigzag oligomers, a polyalkyleneoxy donating group was employed as solubilizing electron-donating endcaps. Alkylation of 4-iodophenol with 1-[2-(2-chloroethoxy)ethoxyl]butane in the presence of $K_2CO_3$ in DMSO yielded the alkylated iodophenol **1**. Palladium-catalyzed Sonogashira coupling of **1** with TMS−acetylene followed by deprotection of the TMS group in a basic medium afforded terminal alkyne **2** in excellent yields (Scheme 1). Double Sonogashira coupling of **2** and 3,6-diiododibenzothiophene *S,S′*-dioxide **5**, which was prepared by iodination of dibenzothiophene **3** with periodic acid/$I_2$ yielding **4** followed by *m*CPBA oxidation,[11] afforded bis-dipolar molecule **DA(2)** in 50% yield. On the other hand, with the use of an excess of **5** over **2** (3:1), the monocoupled compound **9** would become the major product with 45−47% yield and **DA(2)** in 22−23% yield (Scheme 2). The monocoupled compound **9** was used to synthesize tetrakis-dipolar chromophore **DA(4)** in which double Sonogashira coupling of **9** and **6**, which was prepared by double Sonogashira coupling of **4** with TMS−acetylene followed by deprotection of the TMS group, affording 68% yield. Because of the reactivity and solubility problems of intermediates, among various possible routes, the slightly soluble hexakis-dipolar molecule **DA(6)** could only be synthesized by the double Sonogashira coupling of **9** and **10**, which was obtained by the coupling of intermediates **7** and **8** as shown in Scheme 2. The monocoupled compound **7** was prepared by the coupling of **4** and TMS−acetylene (3:1) giving the desired product in 50−60% and the dicoupled product in 25−30% yields; on the other hand, double Sonogashira coupling of **4** and TMS−acetylene, followed by *m*CPBA oxidation and deprotection afforded **8** in 92% yield.

To enhance the intramolecular charge transfer of zigzag chromophores, various central aryleneethynyl units including phenylethynyl, 9,9-dibutylfluorenylethynyl, bis(9,9-dibutylfluorenyl)ethynyl, ter(9,9-dibutylfluorenyl)ethynyl, bithienylethynyl, and terthienylethynyl, which are denoted by MP, MF, DF, TF, DTP, and TTP, respectively, were incorporated to extend the

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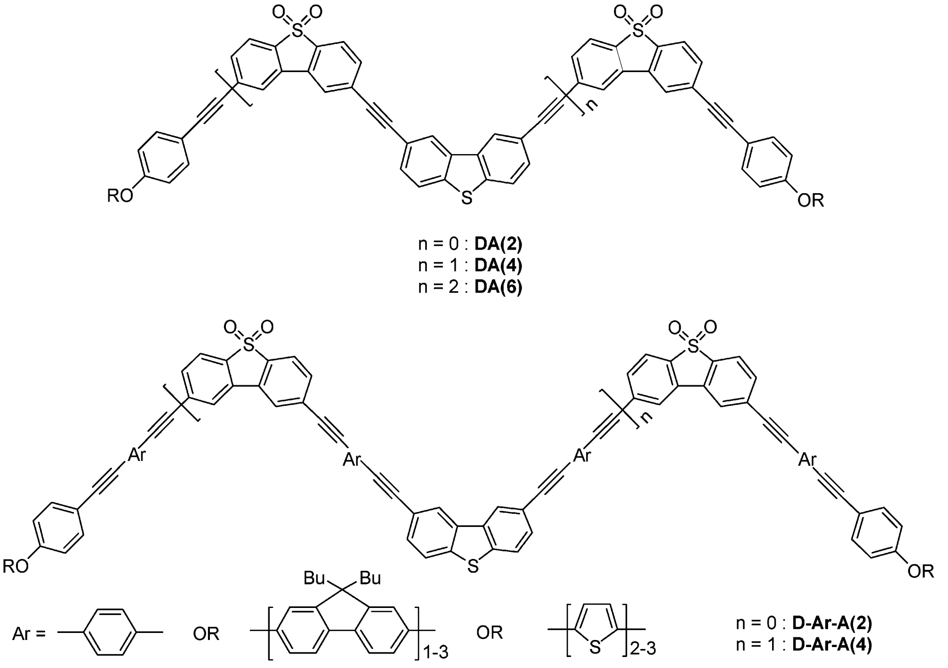
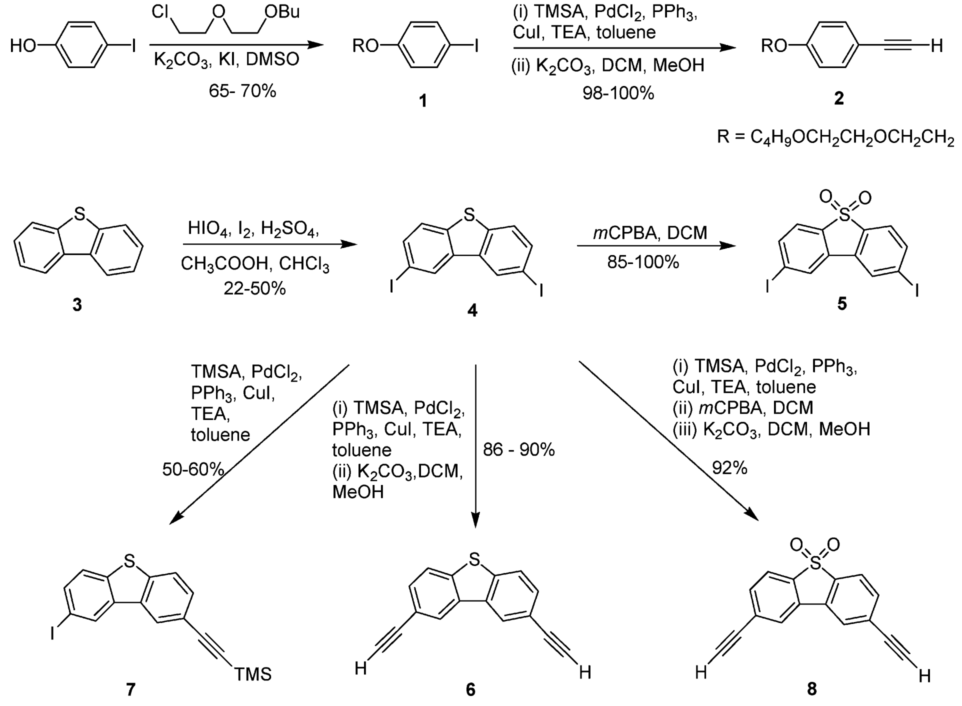
**CHART 1. Molecular Structures of Multi-Dipolar Zigzag Oligoaryleneethynylenes DA(*n*) and D-Ar-A(*n*)**



**SCHEME 1. Synthesis of Intermediates for Multi-Dipolar Zigzag Oligoaryleneethynylenes**



$\pi$-conjugated path. Adopting the same synthetic strategy of **DA(2)**, the extended bis-dipolar zigzag chromophores **D-Ar-A(2)**, where Ar = MP, MF, DF, TF, DTP, and TTP, were synthesized accordingly by means of the double Sonogashira coupling of 3,6-diiododibenzothiophene *S*,*S*′-dioxide **5** with the extended terminal alkynes **12a**−**f**. These extended alkynes were generally prepared by the monocoupling of diiodo-(oligo)arylene with **2** and then with TMS−acetylene followed by TMS-deprotection affording the desired alkynes in 66−97% yields as shown in Scheme 3. As the preparation of the extended analogues of **6** was not so trivial and efficient, an alternative approach was developed for the extended tetrakis-dipolar zigzag chromophore series, **D-Ar-A(4)**, rather than adopting the synthetic strategy of **DA(4)**. Double Sonogashira coupling of **8** and 1,4-diiodophenylene or diiodooligo-9,9-dibutylfluorenes[15] afforded **13a**−**d** in moderate to excellent yields. Monocoupling of **13a**−**d** and **2** (3:1) gave **14a**−**d**, respectively, in 45−65% yield. Again, double Sonogashira coupling of **6** and the monocoupled **14a**−**d** yielded the desired products **D-Ar-A(4)** where Ar = MP, MF, DF, and TF, respectively, in moderate

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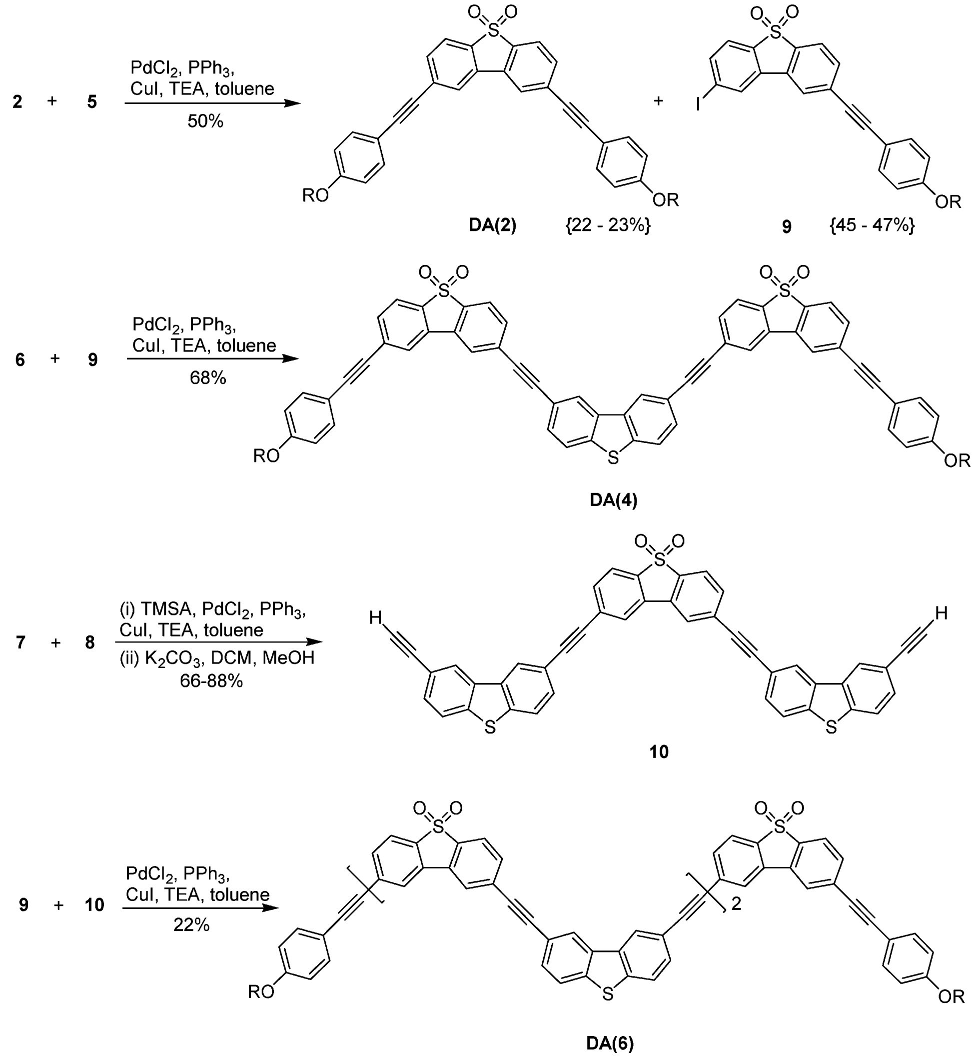
**SCHEME 2. Synthesis of Multi-Dipolar Zigzag Oligoaryleneethynylenes DA(2), DA(4), and DA(6)**



yields (Scheme 3). All the newly synthesized multi-dipolar zigzag oligoaryleneethynylenes were fully characterized by ${}^{1}$H NMR, ${}^{13}$C NMR, and high-resolution mass spectroscopy and elemental analysis and found to be in good agreement with the expected structures.

In view of the absorption spectra of these zigzag oligomers, there is no significant shift in the absorption maxima ($\lambda_{max}^{abs}$) upon an increase in the number of charge-transfer (dipolar) units within a zigzag oligoaryleneethynylene even though the absorption bands are broadened and the molecular absorptivities are enhanced, for example, $\lambda_{max}^{abs} = 345$ nm for **D-MP-A(2)** and 345 nm for **D-MP-A(4)** in $CH_2Cl_2$ and $\lambda_{max}^{abs} = 344$ nm for **D-MP-A(2)** and 342 nm for **D-MP-A(4)** in DMF (Figure 1 and Table 1).

On the other hand, the $\lambda_{max}^{abs}$ shift to longer wavelengths upon an incorporation of various central aryleneethynyl cores such as phenylethynyl, oligo(9,9-dibutylfluorenyl)ethynyl, and oligothienylethynyl varying from 341 nm for **DA(2)** to 373 nm for **D-DF-A(2)** and to 425 nm for **D-TTP-A(2)** in $CH_2Cl_2$ (Figure 2) which is attributed to the enhanced $\pi$-conjugation within the dipolar unit.

All the emission spectra of these multi-dipolar zigzag oligoaryleneethynylenes show moderate to strong positive solvatochromic effect (e.g., **D-MP-A(*n*)**: $\lambda_{max}^{em} = 466$ nm in $CH_2Cl_2$ to 510 nm in DMF; and **D-TF-A(*n*)**: $\lambda_{max}^{em} = 498$ nm in $CH_2Cl_2$ to 544 nm in DMF) suggesting a strong charge-transfer character in the excited state. Generally, the emission spectra of these oligoaryleneethynylenes are also independent of the number of dipolar units linked (Figure 1 and Table 1). Consistently, the emission maxima ($\lambda_{max}^{em}$) are greatly red-shifted upon extending with various central aryleneethynyl cores from 440 nm for **DA(2)** to 483 nm for **D-DF-A(2)** and to 553 nm for **D-TTP-A(2)** in $CH_2Cl_2$ (Figure 3). On the other hand, the fluorescence quantum efficiencies ($\phi_{FL}$) of these oligoaryleneethynylenes decrease slightly when the dipolar units increase from two to four within a molecule (i.e., $\mu_{FL}$ of **D-MF-A(2)** $= 0.86$ vs $\mu_{FL}$ of **D-MF-A(4)** $= 0.72$ and $\mu_{FL}$ of **D-TF-A(2)** $= 0.40$ vs $\mu_{FL}$ of **D-TF-A(4)** $= 0.32$), which is attributed to the neighboring quenching. Interestingly, the $\phi_{FL}$ values can be greatly enhanced by incorporation of phenylethynyl, 9,9-dibutyl-

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(14) Examples of large TPA cross-sections measured using the femtosecond laser pulse as an excitation source at 800 nm in the literature. *N,N,N*-Tris(4-(1-cyano-1-(4-cyanophenyl)vinyl)phenyl)amine: $\sigma_{800} = 790$ GM (Z-scan method).[7c] 4,7,12,15-Tetrakis((4‴-(4″,4′-dihexylaminostyryl)styryl)styryl)[2.2]paracyclophane: $\sigma_{800} = 3200$ GM (TPEF).[7e] 4,4′-[(9,9-Dinonyl-9*H*-fluorene-2,7-diyl)bis[(1*E*)-2,1-ethenediyl-4,1-phenylene-(1*E*)-2,1-ethenediyl]]bis(*N,N*-dihexylbenzenamine): $\sigma_{800} = 1200$ GM (TPEF).[6g]

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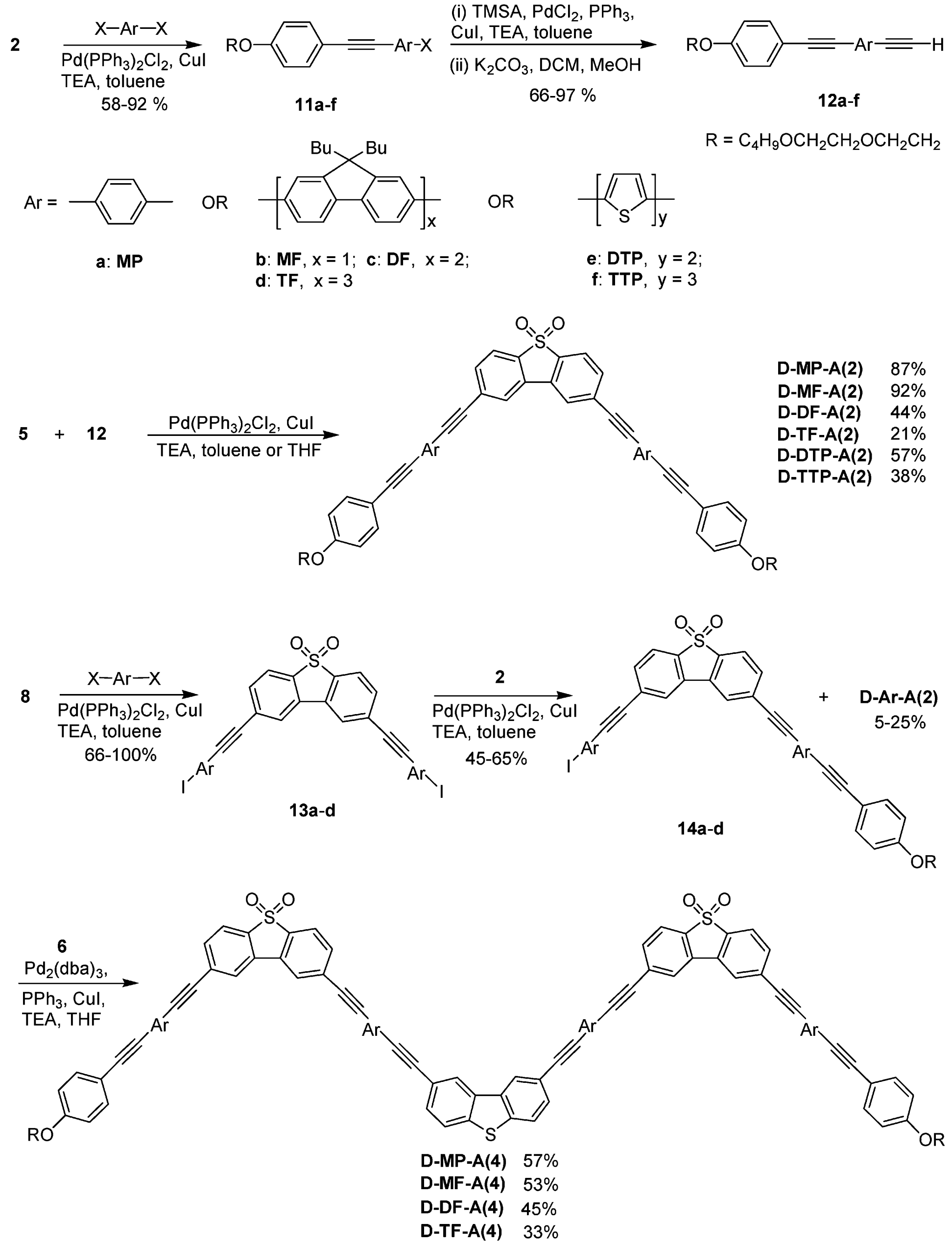
**SCHEME 3. Synthesis of Extended Multi-Dipolar Zigzag Oligoaryleneethynylenes D-Ar-A(*n*)**



fluorenylethynyl, and bis(9,9-dibutylfluorenyl)ethynyl as a central extending bridge but are moderately reduced with a bithienylethynyl and a terthienylethynyl bridge. The $\phi_{FL}$ values of **DA(*n*)** compounds show no significant solvent effect due to their moderate charge-transfer character; however, those of the extended oligoaryleneethynylenes, **D-Ar-A(*n*)** compounds, are greatly reduced in polar solvent as shown in Table 1. The strong charge-transfer character of **D-Ar-A(*n*)** compounds in polar DMF solvent could lead to excitonic coupling, which is detrimental to the $\phi_{FL}$.[12]

The thermal properties of the zigzag oligoaryleneethynylenes were examined by thermogravimetric analysis (TGA). All the zigzag oligomers showed very good thermal stabilities with decomposition temperatures ($T_d$) in the range of 329−429 °C except for **DA(6)**.

The two-photon cross-sections ($\delta$) were determined by the two-photon induced fluorescence method,[13] using a femtosecond pulsed laser as an excitation source in both $CH_2Cl_2$ and DMF. The results of two-photon absorption cross-sections measured at 800 nm are given in Table 1. Compared with the one-photon emission spectra, the two-photon excited fluorescence (TPEF) spectra consistently show a small red-shift likely due to the reabsorption effect with a typical example shown in Figure 4a suggesting that their emissive states might be very similar. In addition to the one-photon excited fluorescence spectra, the two-photon excited fluorescence spectra do not depend on the number of linked dipolar units.

Generally, there is a progressive increase in the TPA cross-sections as the central aryleneethynyl core within the dipolar unit of these zigzag oligoaryleneethynylenes changes from phenylethynyl, 9,9-dibutylfluorenylethynyl, bithienylethynyl, bi-(9,9-dibutylfluorenyl)ethynyl, terthienylethynyl to ter(9,9-dibutylfluorenyl)ethynyl with $\sigma_{800}$ of **D-TF-A(4)** up to 1214 GM in

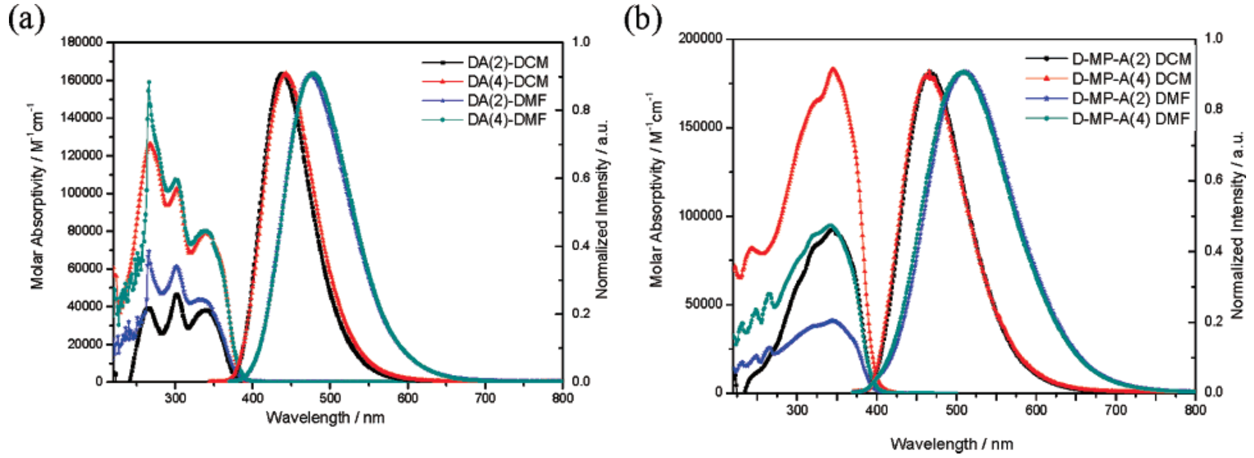


**FIGURE 1.** Absorption spectra ($10^{-6}$ M) and normalized emission spectra ($10^{-7}$ M) excited at 341 and 345 nm, respectively, of (a) **DA(*n*)** and (b) **D-MP-A(*n*)** in $CH_2Cl_2$ and DMF, respectively.

**TABLE 1.** **Summaries of Physical Measurements of DA(*n*) and D-Ar-A(*n*) Series**

| | $\lambda_{max}^{abs}$ $^a$/nm | $\lambda_{max}^{em}$ $^{a,c}$/nm | $\Phi_{FL}$ $^a$ | $\sigma_{800}$ $^{a,g}$/GM | $\lambda_{max}^{abs}$ $^b$/nm | $\lambda_{max}^{em}$ $^b$/nm | $\Phi_{FL}$ $^b$ | $\sigma_{800}$ $^{b,g}$/GM | $T^h$/°C |
|---|---|---|---|---|---|---|---|---|---|
| **DA(2)** | 302, 341 | 440 | 0.45[d] | | 301, 331 | 478 | 0.42[d] | | 360 |
| **DA(4)** | 302, 341 | 443 | 0.37[d] | | 300, 331 | 477 | 0.37[d] | | 371 |
| **DA(6)** | 299, 341 | 446 | 0.22[d] | | 299, 334 | 476 | 0.19[d] | | 194 |
| **D-MP-A(2)** | 345 | 466 | 0.86[d] | 24.5 | 344 | 510 | 0.18[d] | 18.6 | 375 |
| **D-MP-A(4)** | 345 | 466 | 0.80[d] | 23.3 | 342 | 509 | 0.17[d] | 37.1 | 354 |
| **D-MF-A(2)** | 364 | 478 | 0.86[e] | 212 | 365 | 415, 503 | 0.13[e] | 233 | 391 |
| **D-MF-A(4)** | 367 | 476 | 0.72[e] | 433 | 364 | 505 | 0.09[e] | 558 | 429 |
| **D-DF-A(2)** | 373 | 483 | 0.74[e] | 378 | 378 | 427, 507 | 0.17[e] | 449 | 399 |
| **D-DF-A(4)** | 374 | 485 | 0.53[e] | 723 | 374 | 511 | 0.15[e] | 795 | 416 |
| **D-TF-A(2)** | 377 | 498 | 0.40[e] | 609 | 380 | 544 | 0.04[e] | 784 | 409 |
| **D-TF-A(4)** | 378 | 499 | 0.32[e] | 1214 | 378 | 544 | 0.05[e] | 1306 | 329 |
| **D-DTP-A(2)** | 405 | 534 | 0.28[f] | 264 | 404 | 574 | 0.12[f] | 326 | 391 |
| **D-TTP-A(2)** | 425 | 553 | 0.30[f] | 465 | 427 | 590 | 0.05[f] | 702 | 400 |

[a] Measured in $CH_2Cl_2$. [b] Measured in DMF. [c] Excited at the absorption maxima. [d] With quinine in 1.0 M $H_2SO_4$ ($\mu_{334} = 0.56$) as a standard. [e] With 9,10-diphenylanthrancene in cyclohexane ($\mu_{360} = 0.90$) as a standard. [f] With fluorescein in 0.1 M NaOH ($\mu_{436} = 0.92$) as a standard. [g] Determined by the two-photon-induced fluorescence method, using 800 nm femtosecond laser pulses with rhodamine 6G as a standard. [h] Determined by thermal gravimetric analyzer with a heating rate of 10 deg/min under $N_2$.

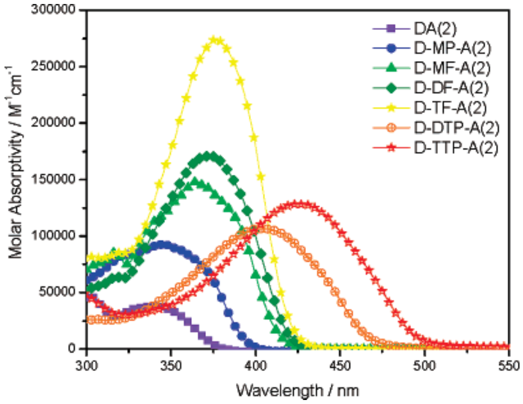


**FIGURE 2.** Absorption spectra of **DA(2)** and **D-Ar-A(2)**s in $CH_2Cl_2$

$CH_2Cl_2$ or 1306 GM in DMF (Table 1), which are attributed to the enhanced electron delocalization and hyperpolarizability of the dipolar unit and the better match of the two-photon absorption wavelength and excitation wavelength. These results indicate that the 9,9-dibutylfluorenylene moiety is more useful than the thienylene moiety to enhance the TPA cross-section. Even though $\phi_{FL}$ values are much smaller in DMF, TPA values measured in DMF are slightly larger than those measured in $CH_2Cl_2$, which is likely due to the enhanced $\pi$-conjugation/charge delocalization in polar solvent. Importantly, upon an increase in the number of dipolar units within a molecule, TPA cross-sections of these zigzag oligomers increase linearly ($\sigma_{800}$ in $CH_2Cl_2$: **D-TF-A(2)** = 609 GM and **D-TF-A(4)** = 1214 GM) without causing the red-shift of absorption and emission. This result suggests that the inter- and intraelectronic couplings of dipolar units are not significant within this zigzag skeleton. This result also implies that varying/increasing the number of dipolar units within a zigzag molecule can provide a means to tune/enhance the TPA cross-section at a specific wavelength such as at 800 nm. Figure 4b shows TPA spectra of **D-Ar-A(4)** measured in $CH_2Cl_2$ in which the maximum of the TPA cross-section seems to be close to twice that of the $\lambda_{max}^{abs}$, suggesting that the lowest energy excited state is both one-photon and two-photon allowed as observed in the typical donor−acceptor molecules. Even though dibenzothiophene and dibenzothiophene dioxide are the moderate electron donor and electron acceptor, respectively, very large TPA cross-sections, $\sigma_{800}$ = 1306 GM in DMF or $\sigma_{750}$ = 1522 GM in $CH_2Cl_2$, were obtained for **D-TF-A(4)**.[14] The power-squared dependence of the two-photon excited fluorescence for these zigzag oligomers was also investigated. In all cases, the power-squared dependence of TPEF was followed with the slope in the range of 1.99−2.04, which directly gives experimental evidence of two-photon excitation nature as shown in Figure 5.

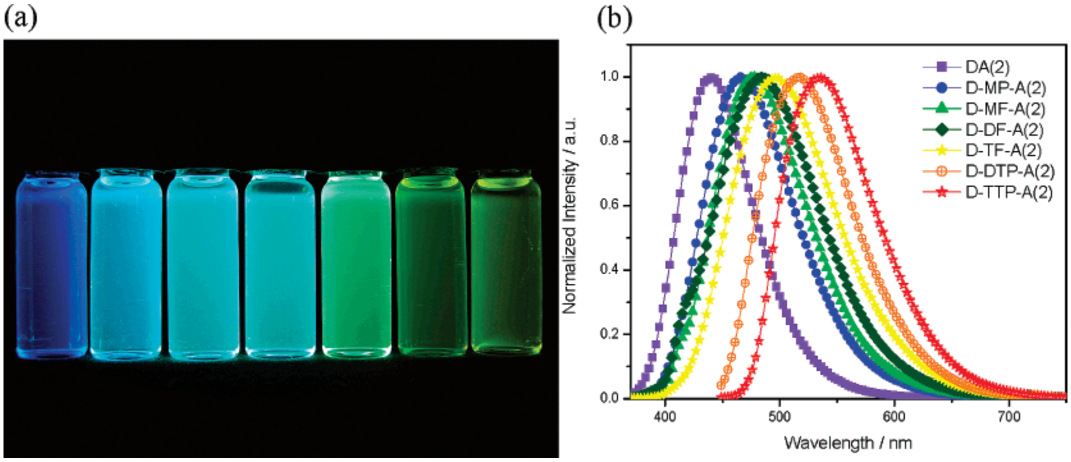


**FIGURE 3.** (a) Luminescence colors upon illumination and (b) emission spectra of **DA(2)** and **D-Ar-A(2)** in $CH_2Cl_2$.

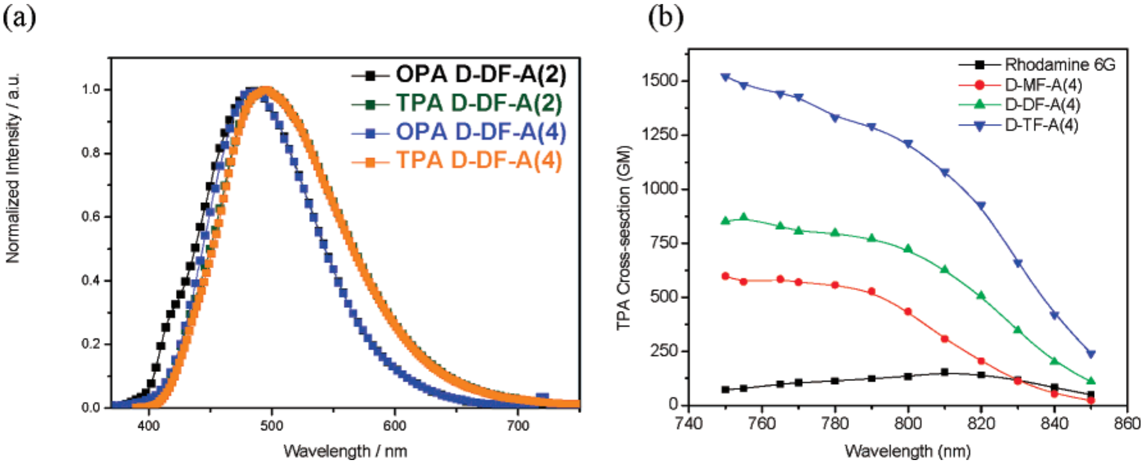


**FIGURE 4.** (a) Comparisons of two-photon excited emission spectra with one-photon emission spectra of **D-DF-A(*n*)**. (b) TPA spectra of **D-Ar-A(4)** (Ar = MF, DF, TF) in $CH_2Cl_2$.

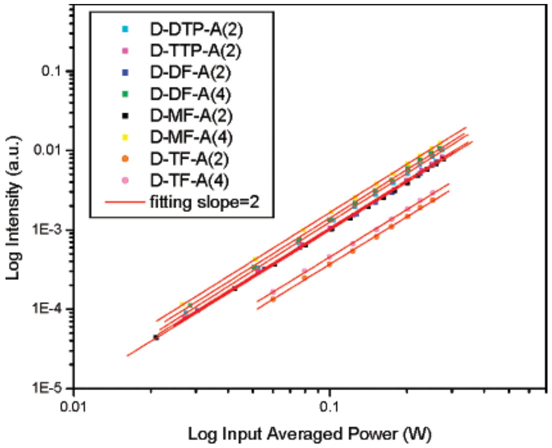


**FIGURE 5.** Logarithmic plots of the power dependence of relative two-photon induced fluorescence on pulse intensity, using an 800 nm femtosecond laser as an exciting source.

## Conclusion

In summary, we have designed and synthesized a novel series of multi-dipolar zigzag oligoaryleneethynylenes **DA(*n*)** and **D-Ar-A(*n*)**, bearing electron-donating dibenzothiophene and electron-accepting dibenzothiophene dioxide as arenes, with up to six charge-transfer (dipolar) units by palladium-catalyzed Sonogashira coupling reactions. The linear/nonlinear optical properties of these multi-dipolar oligoaryleneethynylenes can easily be modified/enhanced by incorporating/ extending with various central aryleneethynyl moieties such as phenylethynyl, oligo(9,9-dibutylfluorenyl)ethynyl, and oligothienylethynyl within the donor−acceptor units. Interestingly, the absorption and emission of these zigzag oligoaryleneethynylenes are not dependent on the number of dipolar chromophores linked; however, the fluorescence quantum efficiencies consistently decrease with increased number of covalently linked dipolar units. Because of the negligible inter- and intrachromophoric interactions, these zigzag oligoaryleneethynylenes exhibit a linear increase in the TPA cross-sections with increased number of covalently linked dipolar units without red-shifting the absorption and emission spectra. Our results suggest that the TPA cross-section can easily be enhanced at a specific wavelength by means of increasing the number of dipolar units within a zigzag molecule. Furthermore, very large TPA cross-sections in the femtosecond regime ($\sigma_{800}$ = 1306 GM in DMF or $\sigma_{750}$ = 1522 GM in $CH_2Cl_2$) were obtained for **D-TF-A(4)**, which shows potential for practical applications. This approach provides an alternative means to tune or enhance the TPA cross-section at a specific wavelength.

## Experimental Section

**General Coupling Procedure: 3,6-Bis(4-{1-[2-(2-butoxyethoxy)-ethoxy]}phenylethynyl)dibenzothiophene Sulfone DA-(2).** To a stirred solution of **5** (0.20 g, 0.43 mmol), $Pd(PPh_3)_2Cl_2$ (12.0 mg, 0.02 mmol), and CuI (1.6 mg, 0.009 mmol) in triethylamine (5 mL) under $N_2$ was added **2** (0.30 g, 1.14 mmol) in dry THF. The reaction mixture was stirred overnight at room temperature under $N_2$. The reaction mixture was extracted with $CH_2Cl_2$ (3 × 30 mL). The combined organic layer was washed with water three times, dried over anhydrous $Na_2SO_4$, and evaporated to dryness. The crude product was purified by silica gel column chromatography with $CH_2Cl_2$/EtOAc (v/v 100:1) as eluent. The pure product was obtained by precipitation from $CH_2Cl_2$/methanol to afford **DA-(2)** as a brownish-orange solid of 0.16 g yield (50%). $^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 7.89 (s, 2H), 7.76 (d, $J = 8.1$ Hz, 2H), 7.61 (d, $J = 9.2$ Hz, 2H), 7.47 (d, $J = 8.9$ Hz, 4H), 6.91 (d, $J = 8.7$ Hz, 4H), 4.16 (t, $J = 4.1$ Hz, 4H), 3.87 (t, $J = 5.4$ Hz, 4H), 3.71 (t, $J = 5.4$ Hz, 4H), 3.59 (t, $J = 5.4$ Hz, 4H), 3.46 (t, $J = 6.8$ Hz, 4H), 1.51−1.66 (m, 4H), 1.31−1.39 (m, 4H), 0.90 (t, $J = 7.3$ Hz, 6H). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 159.5, 136.4, 133.3, 133.1, 131.3, 129.8, 124.2, 122.1, 114.8, 114.2, 93.8, 86.6, 71.2, 70.9, 70.1, 69.5, 67.5, 31.6, 19.2, 13.9. MS (FAB) $m/z$ 736.9 ($M^+$). HRMS (MALDI-TOF) $m/z$ calcd for $C_{44}H_{48}O_8SNa$ 759.2968, found 759.3004 $[M + Na]^+$. Anal. Calcd for $C_{44}H_{48}O_8S$: C, 71.71; H, 6.57. Found: C, 71.62; H, 6.35.

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**Supporting Information Available:** General experimental details, synthetic procedures and spectral data, and copies of $^1H$ NMR and $^{13}C$ NMR spectra of **DA(*n*)** and **D-Ar-A(*n*)** compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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