A Controlled, Iterative Synthesis and the Electronic Properties of Oligo[(*p*-phenyleneethynylene)-*alt*-(2,5-siloleneethynylene)]s

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Abstract: An introductory series of conjugated siloleneethynylene co-oligomers has been prepared from a key 2-chloro-5-iodosilole intermediate via site-specific cross-coupling reactions. The tetramer (**9**) and pentamer (**10**) both exhibit absorption maxima matching those of the corresponding silole copolymers. Extinction coefficients for the oligomers in this series are large, and in the case of the pentamer (**10**) the value exceeds 180 000 M^{-1} cm^{-1}. The compounds all emit in the visible region with the greatest quantum efficiencies being 8.97×10^{-2} (monomer) and 2.99×10^{-2} (pentamer).

Introduction

The synthesis and study of novel chromophores is essential to the expansion and advancement of organic electronic and sensor materials science. There are often synthetic advantages to the preparation of polymeric π-conjugated systems, but frequently existing technologies for their preparation lack the precision required for securing exact chain lengths or controlling site-specific functional group installation. In this regard, an exciting approach to gaining fundamental information into the properties of polymers is the investigation of a discrete set of corresponding oligomeric chromophores of precise length and composition.[1] The challenges inherent to selective oligomer preparation have attracted the attention of synthetic chemists for decades, and important contributions have appeared in the areas of thienylene,[1a] phenylene,[2] and other arylene oligomers.[1b,3]

In contrast, procedures for the preparation of well-defined oligomeric silole chromophores have remained elusive. This is surprising given that conjugated silole networks have potential applications in a wide range of areas including electroluminescence,[4] photoluminescence,[5] and nitroaromatic sensor technologies.[6] Silole polymers rich in acetylenic functionality are particularly interesting because they display unusually narrow band gaps for alkyne-rich systems.[7] The study of oligomeric silole-acetylene systems will provide insight into the structural, thermal, morphological, and electronic properties as a function of chain length.

Phenyleneethynylene oligomers and macrocycles have been prepared by regiospecific alkynylations with aryl triazenes as masked iodoarenes[8] and through the use of aromatics bearing combinations of halide and/or triflate functionality.[9] The former route using Moore's MeI-induced triazene decomposition[8] has not been applied to substrates bearing silole rings in the chromophore. Likewise, the latter approach had not been developed for silole chemistry prior to our recent work on donor–acceptor siloles.[10]

The availability of 2,5-dibromosiloles (e.g., **1**) opened the door to π-conjugated polymeric acetylenic siloles through transition metal-catalyzed cross-coupling reactions.[11] In 1997, Barton and co-workers reported the synthesis of silole-acetylene polymers **2** and **3** (Figure 1).[12] In comparison with poly-(phenyleneethynylene)s ($\lambda_{max} = 425$ nm)[13] and poly(thiophene-

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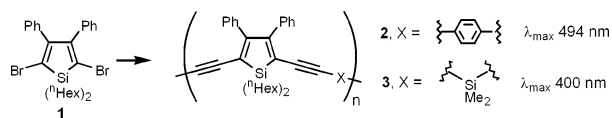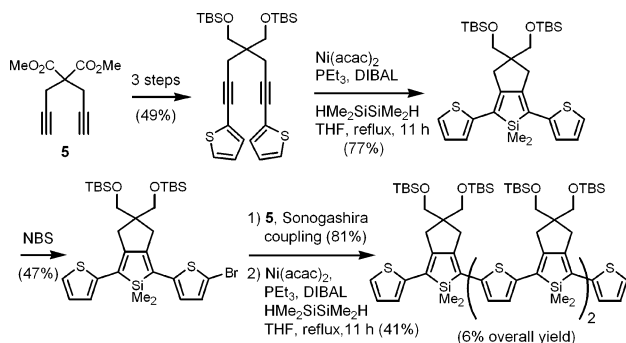
Figure 1. Examples of Barton's silole-containing polymers. Absorption data for polymers in THF at room temperature.
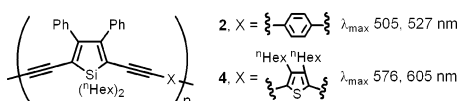
Figure 2. Examples of Tamao's silole-containing polymers. Absorption data for polymers in CHCl$_3$ at room temperature.
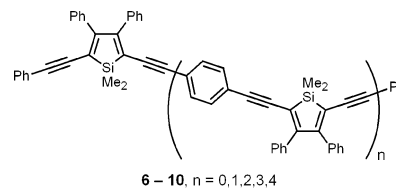
Scheme 1

ethynylene)s (λ_{max} = 438 nm),[14] the silole moiety was strongly implicated as responsible for the dramatically red-shifted absorptions observed with these polymers.

In 1998, Tamao and co-workers reported silole polymers of similar composition (Figure 2).[15,16] Additionally, Tamao examined diethynylthiophene linkages (**4**) and observed an additional red-shift in the absorption spectrum. These remarkable materials are novel examples of alternating copolymers incorporating the electronically unique silole ring.

The synthesis of length-specific oligomers requires the use of an asymmetric building block that can serve either as an end cap or as a starting point for iterative chain extension. Cross-coupling-based strategies for the synthesis of acetylene containing oligomers frequently employ intermediates fitted with orthogonal alkyne protecting groups (e.g., Me$_3$Si vs ^{i}Pr$_3$Si vs Me$_2$COH).[17] However, the use of these venerable protecting groups in the presence of siloles is prohibited due to the greater reactivity of the silole ring under the reaction conditions currently developed for alkyne liberation.[4f,15] In pioneering investigations, Tamao circumvented the obstacle of silole desymmetrization and successfully prepared asymmetric siloles and silole-containing oligomers by manipulation of pendant thiophenes[18] and pyrroles (Scheme 1).[19]

Results and Discussion

Construction of the Oligomer Series. In this paper, we report the synthesis of a structurally homologous family of novel oligomeric silolene chromophores (Figure 3), and we describe their electronic and physical properties as a function of conjugation length. Challenges confronting this endeavor were the lack of an efficient and practical method for preparing

Figure 3. Novel silole oligomers **7**–**10**, and parent silole **6**.

Scheme 2
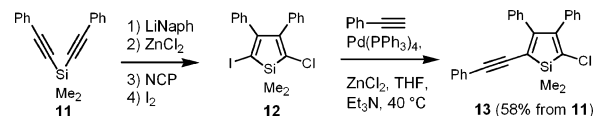
asymmetrical siloles and the limited number of silole-compatible alkyne protecting groups. These were overcome by a direct and efficient synthesis of a mixed halo silole, optimized in situ regiospecific cross couplings, and the employment of terminal alkyne coupling partners when necessary.

We recently described a new process for the efficient formation of and selective cross-coupling reactions with the novel asymmetric chloroiodosilole **12**.[10] In this paper, we illustrate the importance and utility of silole **12** as a powerful intermediate for oligomeric silole synthesis through its deployment as a precursor for all of the asymmetrical siloles described herein. The first crucial building block **13** was obtained in 58% overall yield from diethynylsilane **11** by selective palladium-catalyzed cross coupling between phenylacetylene and chloroiodosilole **12** (Scheme 2).

It is worth noting that cross-coupling reactions performed under Stille[20] or traditional Negishi[21] conditions (i.e., use of preformed alkynylstannane or zinc acetylide, respectively) provided the desired compound in comparable yield. However, Sonogashira[22] conditions gave fickle results, and successful cross-coupling attempts were only observed when Et$_3$N or PhCH$_3$/Et$_3$N solvent systems were used. THF/Et$_3$N solvent systems led to complex reaction mixtures from which no identifiable products or starting materials could be isolated.[23]

Having secured an efficient and scaleable route to the silole "end cap" **13**, we continued the oligomer syntheses by preparation of symmetric infill pieces for the central domain. For oligomers with even numbers of siloles, 1,4-diethynylbenzene was an obvious key building block, and dimeric silole **7** was prepared by standard cross-coupling techniques (Scheme 3).

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(16) Polymer **2** was found in this case to have an absorption maximum at 505 nm, in contrast to 494 nm in Barton's studies. This slight discrepancy can likely be ascribed to different solvents.

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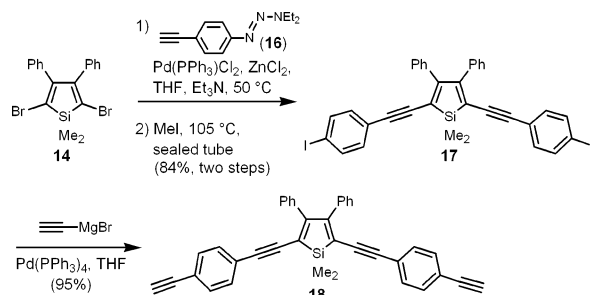
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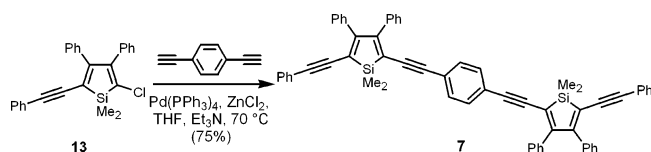
Scheme 4
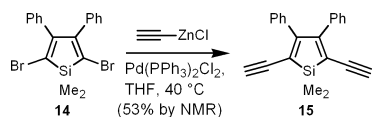
Scheme 5

Scheme 6

Scheme 7

For the synthesis of the odd numbered oligomers, we initially set out to use the simple diyne **15** made from cross coupling with dibromide **14**[10,11b] (Scheme 4). However, compound **15** was only stable in solution, and concentration resulted in the formation of an insoluble brown powder. We note that other siloles bearing terminal alkynes directly attached to the silole ring also exhibited poor stability.[24] We therefore shifted our focus to the preparation of a more robust building block amenable to long-term storage.

Cross-coupling of dibromide **14** with aryl alkyne **16**[25] followed by MeI-induced triazene decomposition[8] provided bis-(iodoarene) **17** in 84% yield for the two steps after purification by recrystallization (Scheme 5). Alkyne extension was achieved by cross-coupling with ethynylmagnesium bromide in the presence of Pd catalyst to give **18**, which was also purified by recrystallization. Gratifyingly, compound **18** has proven to be bench-stable in the solid state for months, and it participates efficiently in cross-coupling reactions (vide infra).
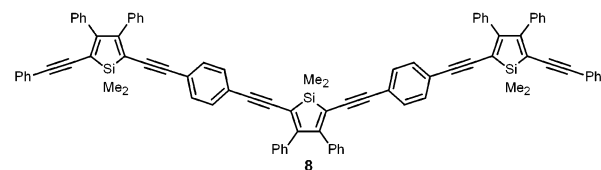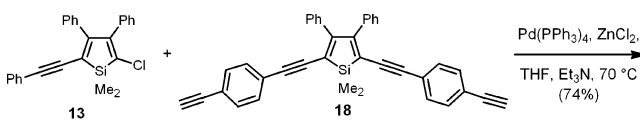
With the end cap **13** and internal silole building block **18** at hand, the trimer **8** was assembled by cross-coupling and purified by recrystallization (Scheme 6). Both dimer **7** and trimer **8** are orange-red powders displaying good solubility in most common organic solvents (e.g., THF, Et$_2$O, CH$_2$Cl$_2$, CHCl$_3$, PhH, DME).

The tetrameric (**9**) and pentameric (**10**) oligomers were constructed using larger end caps that were assembled by synthetic methods similar to those described above, with only minor sequence modifications (Scheme 7). Reaction of chlorosilole **13** with aryl triazene **16** followed by MeI gave iodoarene **19** in 83% yield for the two steps after recrystallization. Cross-coupling with ethynylmagnesium bromide provided terminal alkyne **20** in 91% yield. Using **20** as the in situ cross-coupling partner with chloroiodosilole **12** provided the extended end cap **21**.

The tetrameric (**9**) and pentameric (**10**) siloles were prepared in 76% and 64% yield, respectively, from end-cap **21** and the appropriate internal silole building blocks (Scheme 8). These oligomers are each red powders exhibiting poor solubility in most organic solvents.[26]

Electronic Absorption and Photoluminescence. The electronic absorption spectra of the oligomer family are shown in Figure 4 and are summarized in Table 1. The effect of chain elongation on absorption wavelength diminishes as expected: dimer **7** shows a 38 nm red-shift in comparison with monomer **6**,[27] from dimer **7** to trimer **8** the $\Delta\lambda_{max}$ contracts to 12 nm, and, finally, there is no change in absorption maxima on going from tetramer to pentamer. Tetramer **9** and pentamer **10** each display an absorption maximum within 2 nm of those reported for the analogous high molecular weight silole-containing polymers (i.e., Figures 1 and 2).[12] That is, this work demonstrates for the first time that the effective conjugation length within the corresponding silole polymers, at least to the degree of accuracy that can be estimated by absorption maxima, is approximately equal to the tetramer **9**. Based on the absorption onset, the band gaps (Table 1) also show a convergence to a low-voltage limit as the chain length approaches that of the pentamer, which matches that reported for the polymer **2** (2.07 eV).[15] The extinction coefficients for the oligomer series are also of interest (Table 1). The trimer, tetramer, and pentamer have extinction coefficients greater than 120 000 M^{-1} cm^{-1}, which makes these compounds promising candidates for photovoltaic applications. To the best of our knowledge, these are the highest molar absorptivities reported for any nonpolymeric
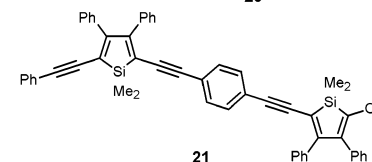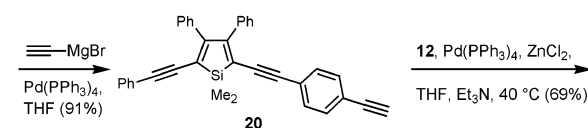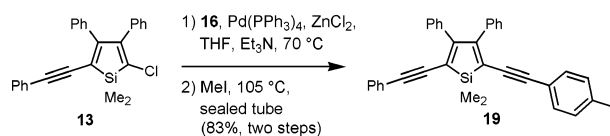
(24) 2-Ethynyl-1,1-dimethyl-3,4-diphenyl-5-(phenylethynyl)silole and 2-chloro-5-ethynyl-1,1-dimethyl-3,4-diphenylsilole were also found to be unstable under the cross-coupling reaction conditions and decomposed upon prolonged storage.

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(26) This is not a general limitation: solubility can be modulated by the use of larger 1,1-dialkyl siloles.

(27) Compounds exactly analogous to **6** have been prepared from 2,5-dibromosiloles; see refs 11b and 15.
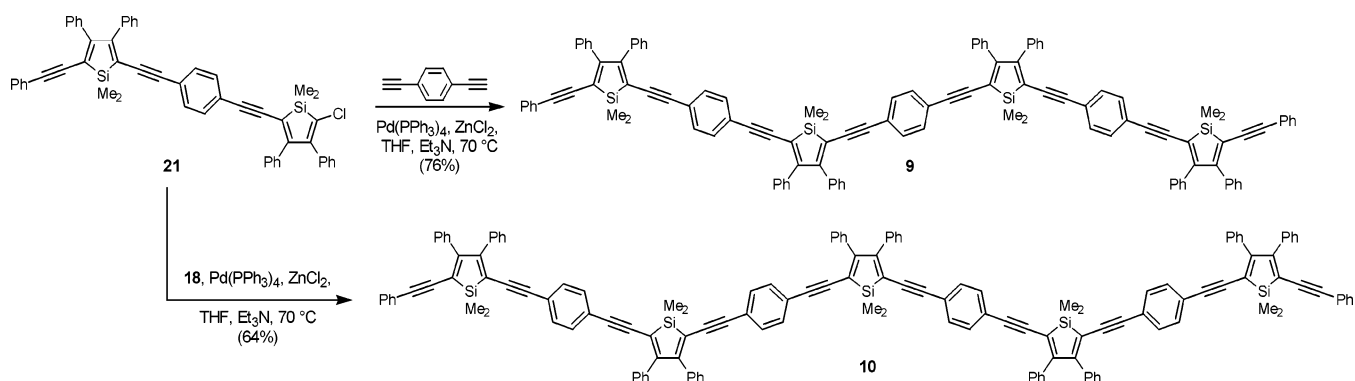
Scheme 8

Table 1. Summary of Electronic Absorption, Emission, and Calculated Bandgap Data for Oligomers

	absorption		emission			
oligomer	λ_{max}	$\log(\epsilon)$	λ_{max}	$\Phi_F{}^a$	$\Delta\lambda_{max}{}^b$	ΔE (eV)^c
monomer (**6**)	429	4.74	520	8.97×10^{-2}		2.43
dimer (**7**)	467	4.85	526	0.26×10^{-2}	38	2.30
trimer (**8**)	479	5.09	543	0.37×10^{-2}	12	2.11
tetramer (**9**)	492	5.17	550	0.22×10^{-2}	13	2.09
pentamer (**10**)	492	5.27	538	2.99×10^{-2}	0	2.08

^{a} Determined with reference to fluorescein. ^{b} Relative to preceding oligomer. ^{c} Estimated from the onset of absorption.
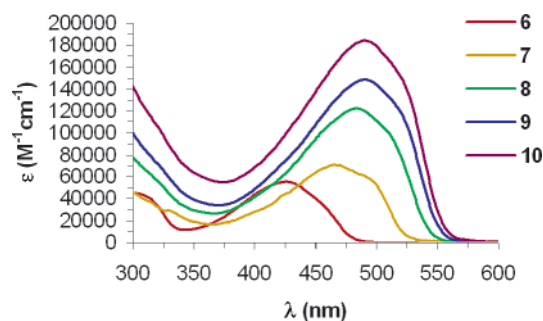
Figure 4. Electronic absorption spectra for the series of first generation silole oligomers in CH_2Cl_2 at room temperature.
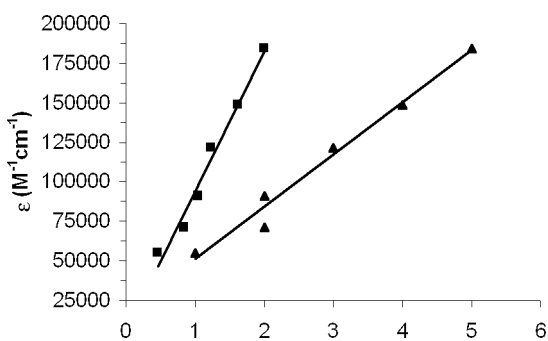
Figure 5. Molar absorptivity as a function of MW $\times 10^{-3}$ (■, $R^2 = 0.98$) and number of silole rings in the chromophore (▲, $R^2 = 0.98$).

silole chromophore. As can be seen in Figure 5, the molar absorptivity increases linearly with the number of silole rings incorporated into the oligomer chain, and with the molecular weights of the oligomers. Thus, this relationship may be useful in estimating the molar absorptivities of silole polymers and higher order oligomers.

The oligomers show modest quantum efficiencies with the monomer being most efficient at 9%, the pentamer next at 3%, and the other oligomers clustered around 0.3%. The modular

nature of the synthetic strategy presented herein will facilitate the optimization of quantum efficiencies through tuning steric interactions.[28] The emission λ_{max} values sequentially red-shift through the series from monomer to trimer (Figure 6, Table 1), at which point increasing conjugation length causes spectrum broadening, but no increase in λ_{max}.

A comparison of these oligomers with the reported properties of non-silole-containing oligo(aryleneethynylene)s reveals that those incorporating siloles display absorption maxima at significantly longer wavelengths (Figure 7). Specifically, at maximum effective conjugation length, the siloleneethynylene oligomers reported herein are more than 50 nm red-shifted with reference to oligo(thienyleneethynylene)s,[29] and greater than 100 nm red-shifted relative to oligo(phenyleneethynylene)s.[30] Note that the basis used in the juxtaposition of these materials' properties was the total number of rings in the chromophore, not the number of repeat units.[31]

The red-shifts observed for the oligomer series reported herein cannot be safely ascribed to the influence of the 3,4-diphenyl functionality as these are known to generally exert a small electronic effect. For example, comparison of silole chromophores **22**−**26** (Figure 8) reveals that for 2,5-dithienyl siloles[32] the inclusion of phenyl rings at the 3,4-position (**24**) results in only a 3 and 9 nm red-shift in comparison with the 3,4-unsubstituted (**23**) and 3,4-dialkyl silole (**22**), respectively. In addition, for 2,5-diphenyl siloles[33] **25** and **26**, substitution at the 3,4-positions (**26**) resulted in a blue-shifted absorption maximum in comparison with the 3,4-unsubstituted silole **25**.

To gain insight into the influence exerted by a single silole ring on the electronic and photoluminescent behavior of an extended chromophore, we synthesized **27** (Scheme 9) for direct comparison with its silole counterpart, trimer **8**. The electronic absorption spectrum of oligomer **27** shows a 33 nm blue-shift of the absorption maximum and a slight decrease in the extinction coefficient (**27** $\lambda_{max} = 446$ nm, $\log \epsilon = 4.96$) resulting from replacement of the center silole with a phenyl ring (Figure 9). The emission λ_{max} is also blue-shifted relative to trimer **8** (Figure 10), but interestingly the quantum efficiency is 20.11×10^{-2} in the case of **27**[34] versus 0.37×10^{-2} for trimer **8**.

(28) These results will be reported elsewhere.
(29) Pearson, D. L.; Schumm, J. S.; Tour, J. M. *Macromolecules* **1994**, *27*, 2348−2350.
(30) Jones, L., II; Schumm, J. S.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1388−1410.
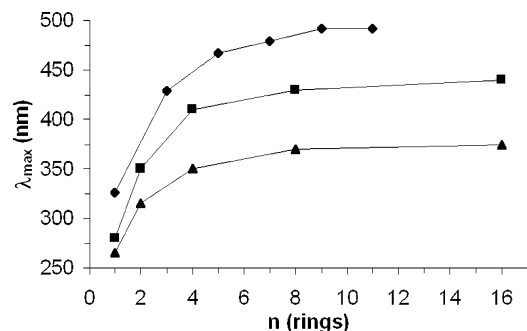(31) For example, pentamer **10** is counted as an 11-mer.
(32) Yamaguchi, S.; Tamao, K. *J. Chem. Soc., Dalton Trans.* **1998**, 3693−3702.
(33) Katkevics, M.; Yamaguchi, S.; Toshimitsu, A.; Tamao, K. *Organometallics* **1998**, *17*, 5796−5800 and references therein.
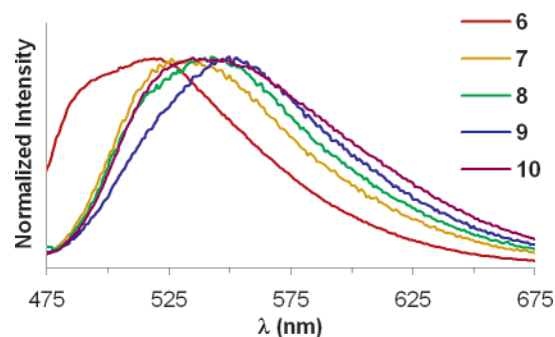
Figure 6. Photoluminescence spectra for the series of first generation silole oligomers in CH_2Cl_2 at room temperature.
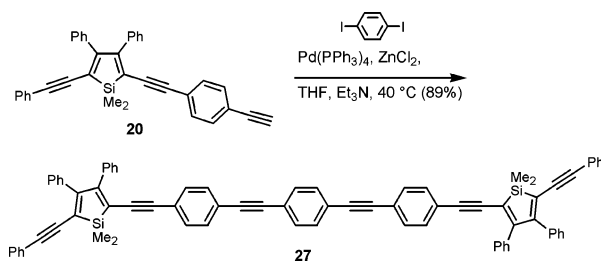

Figure 7. Absorption maxima as a function of rings in the backbone for the alternating silole-containing co-oligomers presented herein (◆), oligo-(thienyleneethynylene)s[29] (■), and oligo(phenyleneethynylene)s[30] (▲).
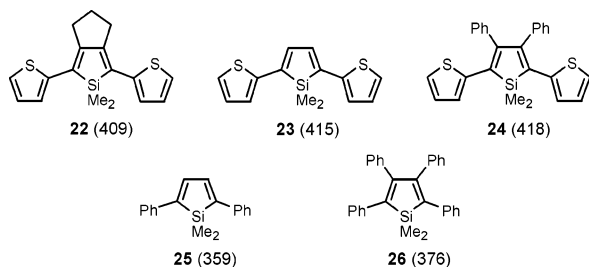
Figure 8. Absorption maxima (nm) in parentheses for the comparison of the effects of differing 3,4-substituents.

Scheme 9

Conclusions

Herein, we have reported the first homologous series of well-defined oligomeric ethynylsilole chromophores and demonstrated the power of synthetic strategies based on 2-chloro-5-iodosilole **12**. The construction of the oligomers centered around direct desymmetrization and derivatization of a silole ring, whereas previous strategies relied on monolithiation or monobromination of pendant aryl groups, or monolithiation of dibromosiloles. This new oligomer synthesis is very practical

(34) Φ_F was determined with reference to fluorescein.
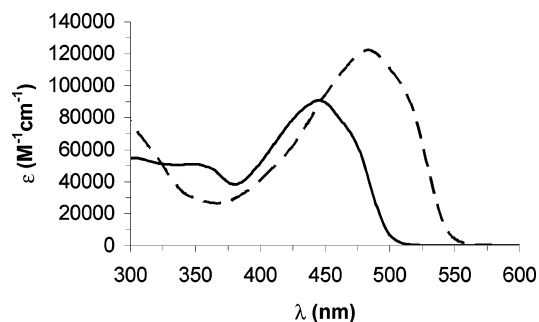
Figure 9. Electronic absorption spectra of trimer **8** (- - -) and **27** (—) in CH_2Cl_2 at room temperature.
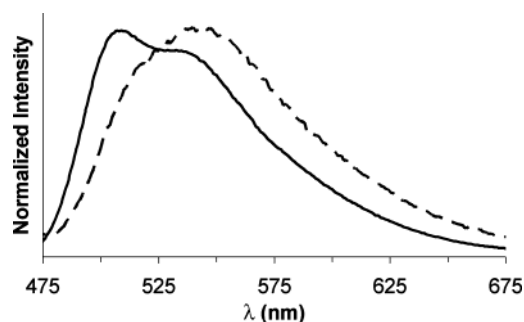
Figure 10. Photoluminescence spectra of trimer **8** (- - -) and **27** (—) in CH_2Cl_2 at room temperature.

overall, requires few synthetic steps, and is highly atom economical. The overall sequence efficiency makes the routes described here amenable to considerable scale-up. Specifically, the oligomers were prepared in excellent overall yield from commercially available diethynyl silane **11**: dimer **7** (44%), trimer **8** (29%), tetramer **9** (23%), and pentamer **10** (13%). The intermediates are generally solids and can be purified by recrystallization alone (only three compounds required chromatographic purification). The fully optimized reaction conditions described in the Supporting Information require no special equipment, strict thermal control, or technical skills beyond experience with anaerobic synthesis.

It is gratifying to observe that the long wavelength absorptions exhibited by these relatively short oligomers imply electronic behavior similar to that of silole polymers reaching molecular weights of 64 000.[12,15] This work establishes for the first time the effective conjugation length in oligo[(*p*-phenylene-ethynylene)-*alt*-(2,5-siloleneethynylene)]s.

We are currently conducting studies on the electroluminescent, electro-generated chemiluminescent, and nonlinear optical properties of these and related compounds.

Supporting Information Available: Detailed experimental procedures and copies of NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

JA047983A