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Cross-Conjugated Chromophores: Synthesis of *iso*-Polydiacetylenes with Donor/Acceptor Substitution[†]

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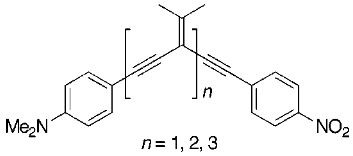
ABSTRACT



The iterative construction of cross-conjugated donor (D), acceptor (A), and donor–acceptor (D–A) substituted *iso*-polydiacetylene (iso-PDA) oligomers has been achieved utilizing palladium-catalyzed cross-coupling techniques. Structure–property relationships for these compounds have been analyzed for cross-conjugated π-electronic communication as a result of contributions from donor, acceptor, or donor–acceptor functionalization.

The delocalized and polarizable π-electron system present in conjugated organic molecules affords many of the physical characteristics necessary for the use of these materials in electronic and photonic applications.[1] A common motif in the study of conjugated systems involves a direct comparison of the electronic effects that result from sequential increases in conjugation length, the so-called oligomer approach.[2,3] The properties of many systems have been further manipulated via attachment of π-electron donor and/or acceptor groups.[4] By using the above approaches, relationships between stability, physical properties, and function have been described for linearly conjugated systems such as, among many others, stilbenes,[5,6] azobenzenes,[7] thiophenes,[4a,b] and polyenes.[4c,5]

Cross-conjugation in organic compounds represents an alternative mode of π-electron communication.[8−10] To date, however, cross-conjugated systems have been largely ignored. Although there are examples of D−A cross-conjugated molecules to be found in the literature,[11] there are very few examples of structurally related series of cross-conjugated chromophores suitable for detailed analysis. As a consequence, fundament knowledge of the effects of D/A interactions in cross-conjugated molecules is quite limited.

In this paper, we report the stepwise, modular synthesis of a new class of cross-conjugated oligomers that have been

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[†] Dedicated to Professor Dr. Henning Hopf on the occasion of his 60th birthday.

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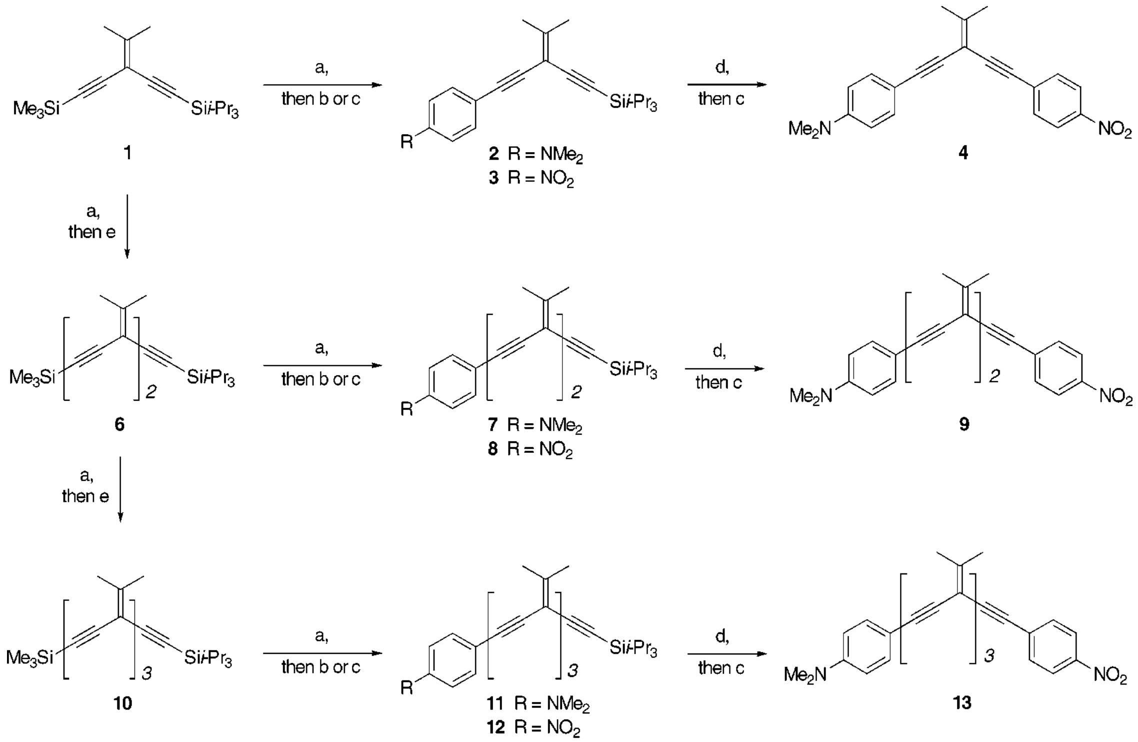
Scheme 1



(a) K_2CO_3, MeOH/wet THF (5:1), rt; (b) *p*-Iodo-*N*,*N*-dimethylaniline, $PdCl_2(PPh_3)_2$, CuI, Et_3N, rt; (c) *p*-Iodonitrobenzene, $PdCl_2(PPh_3)_2$, CuI, Et_3N, THF, rt; (d) TBAF, wet THF, rt; (e) **5**, $Pd(PPh_3)_4$, CuI, Et_2NH, DMF, rt.

selectively end-capped with the *p*-*N*,*N*-dimethylaminophenyl (donor) and/or *p*-nitrophenyl (acceptor) groups. Preliminary analysis of the electronic absorption characteristics indicates that D−A interactions are possible in the smallest of these chromophores (monomer **4**). Analogous D−A communication is, however, limited for the longer oligomers **9** and **13**, for which little change in electronic behavior is observed as a result of increased oligomer length.

The series of cross-conjugated chromophores was synthesized beginning from the differentially protected enediyne **1** (Scheme 1).[10] Protodesilylation of **1** with K_2CO_3 in wet MeOH/THF (5:1) effected removal of the trimethylsilyl (TMS) moiety, while leaving the more robust triisopropylsilyl (TIPS) protecting group intact. This monodesilylated derivative was then carried on directly, following workup, to a Pd-catalyzed cross-coupling with *p*-iodo-*N*,*N*-dimethylaniline[12] to afford the donor-substituted monomer **2** in 63% yield. The analogous sequence of protodesilylation and cross-coupling of deprotected **1** with *p*-iodonitrobenzene gave acceptor-substituted monomer **3**.[13] As the precursor to D−A monomer **4**, we chose to use donor-substituted **2** with the expectation that the cross-coupling of **2** with electron-deficient 4-iodonitrobenzene would be easier than the coupling of **3** with the 4-iodo-*N*,*N*-dimethylaniline. Thus, treating a THF solution of **2** with a slight excess of tetrabutylammonium fluoride (TBAF) effected removal of the TIPS moiety, and cross-coupling with *p*-iodonitrobenzene provided D−A-substituted monomer **4** as an orange solid.

The assembly of longer D/A oligomers began with the common building block **1**. Following desilylation of **1**, cross-coupling with vinyl triflate **5**[14] utilizing $Pd(PPh_3)_4$/CuI and Et_2NH in DMF gave iso-PDA dimer **6**.[10] Selective removal of the TMS moiety of **6**, followed by cross-coupling of the relatively unstable intermediate with *p*-iodo-*N*,*N*-dimethylaniline or *p*-iodonitrobenzene gave **7** and **8**, respectively.[15] TIPS removal from **7** with TBAF provided the terminal

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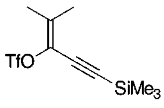
(15) **Typical Procedures. Preparation of 6, 7, and 9.** K_2CO_3 (30 mg, 0.22 mmol) was added to a solution of **1** (151 mg, 0.455 mmol) in wet THF (5 mL) and MeOH (15 mL) and reacted for 2 h. Et_2O and H_2O were added, and the organic phase was separated, washed with aqueous NH_4Cl, dried ($MgSO_4$), and reduced in vacuo to ca. 5 mL. The desilylated compound was added to a degassed solution of **5** (109 mg, 0.365 mmol) in DMF (10 mL). $Pd(PPh_3)_4$ (21 mg, 0.02 mmol) and Et_2NH (3 mL) were sequentially added. After the solution stirred for 5 min, CuI (10 mg, 0.06 mmol) was

alkyne that was then coupled with *p*-iodonitrobenzene to give the D−A dimer **9** as an orange solid.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To complete this series of cross-conjugated chromophores, dimer **6** was selectively protodesilylated and cross-coupled with vinyl triflate **5** to give the trimer **10** in 52% yield. Donor- and acceptor-substituted trimers **11** and **12** were synthesized in good yields by desilylation of **10** followed by coupling with *p*-iodo-*N*,*N*-dimethylaniline and *p*-iodonitrobenzene, respectively. Desilylation of donor **11** and cross-coupling with *p*-iodonitrobenzene afforded D−A-**13** in 70% yield as an orange solid.

Thermally, donor/acceptor oligomers **4**, **9**, and **13** show reasonable stability despite their potentially reactive enyne framework. Melting points for all derivatives are found in Table 1, as are decomposition points for D−A derivatives **4**, **9**, and 1**3** as determined by differential scanning calorimetry.

Table 1. Selected Physical Data for D/A *iso*-PDAs

compound	% yield	$\lambda_{\max}$ (ϵ)^a	mp (°C)^b
2	63	325 (21 000)	45−46
3	83	351 (15 600)	70−72
4	70	325 (34 000)	159−162 227 (dec)^c
7	56	325 (26 100) 303 (35 700) 295 (34 800)	68−69
8	92	358 (12 500) 303 (23 100) 293 (24 600)	58−60
9	76	325 (sh, 31 300) 291 (43 500)	154−156 217 (dec)^c
11	76	325 (sh, 24 800) 295 (38 600)	111−113
12	84	352 (9 800) 307 (sh, 22 900) 287 (26 600)	77−79
13	75	325 (35 500) 297 (46 600)	147 (dec)^c

^{a} In $CHCl_3$; ϵ in L mol^{-1} cm^{-1}. ^{b} Uncorrected. ^{c} Decomposition, by DSC.

Empirically, the most obvious electronic changes are observed within the series of monomers **2**−**4**. As a result of donor−acceptor substitution, monomer **4** is clearly a more highly colored orange solid in comparison to donor (**2**) and acceptor (**3**) monomers, which are yellow solids. In the absence of cross-conjugated D−A interactions across the alkylidene spacer, one expects the spectrum of **4** to merely be a composite of its parts, i.e., **2** and **3**. The difference between the more colored **4**, versus **2** and **3**, is found in the lower energy region of the spectrum that extends out beyond 450 nm for **4** (Figure 1a). At this point, however, it is impossible to determine if this difference results from a red-shifted absorption band for **4** or from "tailing" of a hidden shoulder absorbance. The UV−vis characteristics of **2**−**4** are similar to those observed for tetraethynylethene derivatives with cross-conjugated D/A substitution.[11a] Their behavior, however, dramatically contrasts that of similar linearly conjugated chromophores, which show significant bathochromic shifts upon D−A substition.[5,6,16]

Donor−acceptor chromophores **9** and **13** are also orange solids, whereas donor (**7**, **11)** and acceptor (**8**, **12)** derivatives

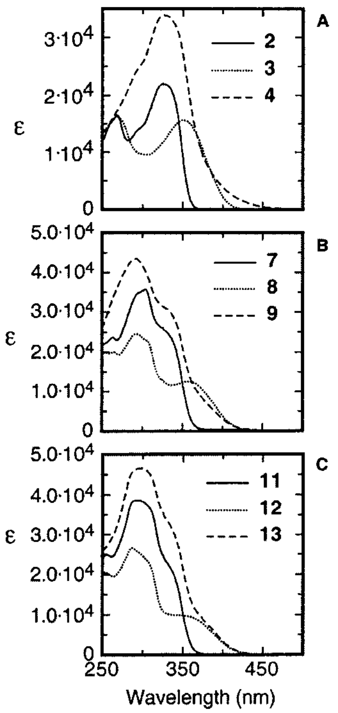

Figure 1. Electronic absorption spectra in $CHCl_3$ comparing (A) monomers **2**−**4**, (B) dimers **7**−**9**, and (C) trimers **11**−**13**.

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added, and stirring was continued under N_2 for 2 h. Workup and column chromatography (silica gel, hexane/CH_2Cl_2 1:1) afforded **6** (118 mg, 63%). To a solution of **6** (152 mg, 0.370 mmol) in wet THF (3 mL) and MeOH (15 mL) was added K_2CO_3 (27 mg, 0.21 mmol), and the mixture reacted for 5 h. Following workup, the ethereal solution of the terminal acetylene was reduced in vacuo to ca. 5 mL and added to a degassed solution of *p*-iodo-*N*,*N*-dimethylaniline (106 mg, 0.482 mmol) in Et_3N (40 mL). $PdCl_2(PPh_3)_2$ (27 mg, 0.04 mmol) and CuI (14 mg, 0.07 mmol) were added, and the mixture was stirred at room temperature under nitrogen for 14 h. Workup and column chromatography (silica gel, hexane/CH_2Cl_2 5:2) afforded **7** (96 mg, 56%). To a solution of **7** (66.4 mg, 0.145 mmol) in wet THF (25 mL) at 0 °C was added Bu_4NF (0.3 mL, 1.0 M in THF), and the mixture stirred for 15 min. Following workup, the ethereal solution of the terminal acetylene was reduced in vacuo to 5 mL and added to a mixture of Et_3N (20 mL) and THF (20 mL). The solution was degassed for 1.5 h, *p*-iodonitrobenzene (36.7 mg, 0.147 mmol), $PdCl_2(PPh_3)_2$ (4.7 mg, 0.007 mmol), and CuI (4 mg, 0.021 mmol) were added, and the mixture was stirred at room temperature under nitrogen for 6 h. Workup and column chromatography (silica gel, hexane/CH_2Cl_2 1:1) afforded **9** (33 mg, 76%) as an orange solid, mp 154−156 °C: IR (cast) 2924, 2202, 1608, 1519, 1342 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (*d*, J = 9.0 Hz, 2H), 7.57 (*d*, J = 9.0 Hz, 2H), 7.32 (*d*, J = 8.9 Hz, 2H), 6.61 (*d*, J = 8.9 Hz, 2H), 2.95 (s, 6 H), 2.12 (s, 6H), 2.10 (s, 3H), 2.08 (m, 3H); ^{13}C NMR (75.5 MHz, C_6D_6) δ 155.4, 151.9, 150.3, 147.1, 133.0, 131.9, 130.0, 123.4, 112.2, 111.0, 103.0, 102.3, 93.6, 92.2, 90.5, 90.0, 87.9, 85.1, 39.6, 22.8, 22.7 (3C); EI HRMS 422.19874 (M$^+$, 100).

are pale and bright yellow solids, respectively. The UV−vis spectra for D/A-substituted dimer **9** and trimer **13** (Figure 1b,c) are similar to those of monomer **4**, with the notable exception that there is no lower energy absorption for **9** and **13**. Thus, only monomer **4** exhibits a UV−vis observable influence from the incorporation donor and acceptor groups to the enyne framework.

In conclusion, we have developed an iterative and versatile procedure for assembling donor and/or acceptor-substituted cross-conjugated enyne oligomers. The electronic characteristics of this new series of oligomers have been studied by UV−vis spectroscopy and show that, whereas D/A monomer **4** shows evidence of D/A electronic communication, such communication in the longer oligomers **9** and **13** appears to be considerably limited.

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Supporting Information Available: Experimental procedures and characterization for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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