Synthesis of Oligoenes that Contain up to 15 Double Bonds from 1,6-Heptadiynes

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Abstract: This paper reports the synthesis of polyene oligomers ("oligoenes") that contain up to 15 double bonds that are identical to the "all five-membered ring" species formed through cyclopolymerization of diisopropyldipropargylmalonate. The oligoenes contain an isopropylidene unit at each end. The isolated oligoenes range from the "dimer" (a pentaene, (*E*)-di-1,2-[1-(2-methyl-propenyl)-4,4-di-*iso*-propyl-carboxy-cyclopent-1-enyl]-ethene (**3b$_2$**)) to the "heptamer" (**3b$_7$**, a pentadecaene). Oligoenes **3b$_2$**, **3b$_3$**, **3b$_4$**, **3b$_5$**, and **3b$_7$** were prepared through Wittig-like reactions between aldehydes and the appropriate monometallic Mo alkylidene or bimetallic Mo bisalkylidene species whose alkylidene is derived from an identical five-membered ring monomeric unit. Compounds **3b$_2$**, **3b$_4$**, and **3b$_6$** were prepared through McMurry coupling reactions of aldehydes. A representative aldehyde (the "monomeric" aldehyde) is diisopropyl-3-formyl-4-(2-methylprop-1-enyl)cyclopent-3-ene-1,1-dicarboxylate (**3**McMurry coupliny of

understanding of the basic photophysics and photochemistry of these systems.[6] One important outcome of the work on simple polyenes was the discovery of a low energy, symmetry forbidden $(1^1A_g^- \rightarrow {}^1A_g^-)$ transition $(S_0 \rightarrow S_1)$ that lies below the strongly allowed $1^1A_g^- \rightarrow 1^1B_u^+$ transition $(S_0 \rightarrow S_2)$ associated with the excitation of an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) in simple versions of molecular orbital theory.[7]

There also is considerable interest in the spectroscopy and photochemistry of longer polyenes and, in particular, how the energies and dynamics of polyene excited states change with increasing ∂-electron delocalization. Naturally occurring polyenes in the form of carotenoids play important roles in photobiology, e.g., in vision and photosynthesis, and their strongly allowed $S_0 \rightarrow S_2$ transitions provide a broad palette of colors to plants and animals. Carotenoids function as light-harvesting pigments in photosynthesis, absorbing light and transferring energy to other antenna pigments and chlorophylls in reaction centers.[8] Carotenoids also play crucial protective roles in these biological systems; their low-energy triplet states quench chlorophyll triplet states, thus preventing irreversible damage due to the photosensitization of singlet oxygen. Synthetic polyenes/oligoenes could play similar roles in artificial photosynthetic systems. Understanding how excited-state energies and lifetimes change with conjugation length and other structural modifications would allow optimization of light harvesting and photoprotection in the design of light-driven, synthetic systems.

Systematic study of the optical and electronic properties of "long" polyenes has been limited to molecules with $N \leq 15$ as a consequence of a lack of synthetic routes to longer polyenes and their limited solubilities. It also is interesting to note that $N \leq 13$ for the longest natural carotenoids such as $\hat{a}$-carotene

(6) Polívka, T.; Sundström, V. *Chem. Rev.* **2004**, *104*, 2021.

$(N = 11)$, lycopene $(N = 11)$, and astaxanthin $(N = 13)$.[9] Much work remains to be done to extend our understanding of the optical properties of the short polyenes and carotenoids to much longer oligomers and ultimately polymers. As mentioned earlier, substituted polyenes tend to suffer from conformational disorder[10] and in some cases regioerrors, which complicate the interpretation of their optical spectra and other electronic properties. Investigation of the optical properties of a range of soluble, planar, regioregular polyenes/oligoenes with known structures would offer critical advantages in relating their optical and electronic properties to conjugation length, geometry, and other variations in molecular structure.

Poly[1,6-heptadiynes] such as poly[dialkyldipropargylmalonates] are highly conjugated and relatively soluble and appear to be relatively stable in air.[4] These polymers were first prepared using "classical" olefin metathesis (alkylidene) catalysts that are prepared from Mo or W halides or oxyhalides and some alkylating agent.[4] In general these polymers do not have a regular structure. As a consequence of addition of the first triple bond to the alkylidene to give either an α- or a $\hat{a}$-substituted metallacyclobutene, both six-membered rings and five-membered rings are usually formed (Scheme 1).

We first explored the polymerization of diethyldipropargylmalonate (DEDPM) and related derivatives with well-defined Mo-based olefin metathesis catalysts, primarily Mo(NAr)-(CHCMe$_2$Ph)(OR$_{F6}$)$_2$ (Ar = 2,6-i-Pr$_2$C$_6$H$_3$, OR$_{F6}$ = OCMe-(CF$_3$)$_2$), in 1992.[11] These studies confirmed that high oxidation state Mo alkylidenes were catalysts for cyclopolymerization reactions of this general type. The resulting polymer formed using Mo(NAr)(CHCMe$_2$Ph)(OR$_{F6}$)$_2$ as the initiator was shown to contain both five-membered and six-membered rings. Later we showed that polyenes that contain all six-membered rings were formed when dicarboxylate catalysts of the type

Mo(N-2-t-BuC$_6$H$_4$)(CHCMe$_3$)(O$_2$CCPh$_3$)$_2$ were employed.[12] DEDPM polymers that contain only six-membered rings have i_{max} values that are lower by 20−30 nm for a given apparent chain length than those for polymers that contain both five- and six-membered rings, consistent with a lower effective conjugation length, presumably as a consequence of twisting of the polymer chain. Buchmeiser and co-workers have shown that Mo(NAr)(CHCMe$_2$Ph)(OCMe$_3$)$_2$ catalysts will polymerize DEDPM to yield polymers that contain >95% five-membered rings.[13] Advantages of poly[1,6-heptadiynes] that contain only five-membered rings include the single alternating *cis*,*trans* structure and the potentially relatively rigid extended chain if conjugation is maintained. Since *all* polymerizations that begin with neopentylidene or neophylidene initiators have a high rate of polymerization versus initiation in polymerizations of this type, we recently prepared initiators that will initiate rapidly relative to the rate of propagation, including one that contains the very type of five-membered ring being formed in a cyclopolymerization reaction, i.e., **1a'** in eq 1.[14] We also showed that **1a** would react with aldehyde **2a** to yield the "dimer", **3a$_2$**, cleanly and 51ere6(5tain)-2ori3

Crystals of **7** suitable for an X-ray crystallographic analysis could be obtained readily. Its structure (Figure 1 and Table 1) is unremarkable and, therefore, is not discussed in detail. Selected distances and angles can be found in Table 2. It should be noted that the isopropyl groups in the imido ligands are turned away from the esters slightly, consistent with some steric crowding.

The difficulty of preparing and handling **6a** prompted us to explore analogues that contain other esters, in particular, isopropyl esters. Compounds **5b** and **6b** (eq 2) proved to be highly crystalline and readily isolated after minimal workup; only passage through a silica gel plug is necessary. In contrast to **6a**, **6b** showed no signs of decomposition upon storage in the solid state under dinitrogen. Interestingly, attempts to isolate the bimetallic isopropyl ester analogue of **7** failed, possibly for
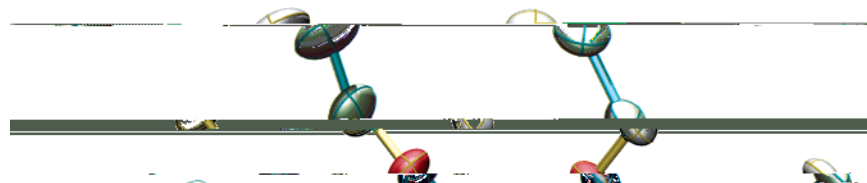
Figure 1. POV-ray rendering (ellipsoids at 50%) of the molecular structure of **7**. Fluorine atoms, hydrogen atoms, and the cocrystallized pentane molecule are omitted for clarity.

Table 1. Crystal Data and Structure Refinement Parameters for **7** and **17**[a]

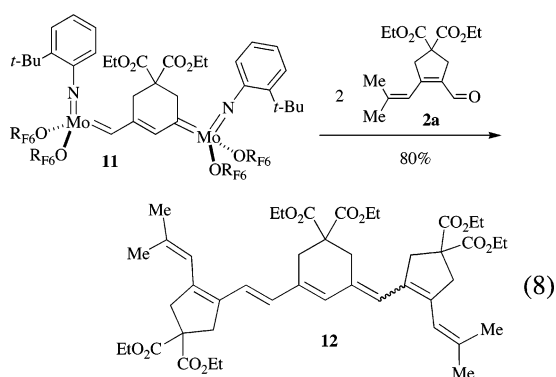| compound	7	17
reciprocal net ident.	**05196**	**05149**
empirical formula	$C_{55.50}H_{68}F_{24}Mo_2N_2O_8$	$C_{79}H_{110}F_{24}Mo_2N_2O_{14}$
formula weight	1539.00	1959.57
crystal system	monoclinic	monoclinic
space group	$P2(1)/n$	$P2(1)/n$
unit cell dimensions	$a = 11.0704(4)$ Å	$a = 10.1034(7)$ Å
	$b = 27.1993(10)$ Å	$b = 29.987(2)$ Å
	$c = 22.5569(9)$ Å	$c = 14.9740(10)$ Å
	$\alpha = \gamma = 90°$	$\alpha = \gamma = 90°$
	$\beta = 90.8330(10)°$	$\beta = 104.099(2)°$
volume	$6791.3(4)$ Å^3	$4400.0(5)$ Å^3
Z	4	2
density (calculated)	1.505 g/cm^3	1.479 g/cm^3
absorption coefficient	0.484 mm^{-1}	0.396 mm^{-1}
$F(000)$	3116	2020
theta range for data collection	1.75° to 28.70°	1.95° to 22.72°
index ranges	$-14 \leq h \leq 14$	$-10 \leq h \leq 10$
	$-36 \leq k \leq 36,$	$0 \leq k \leq 32$
	$-30 \leq l \leq 30$	$0 \leq l \leq 16$
reflections collected	135 769	57 906
independent reflections	17 523 [R(int) = 0.0699]	5908 [R(int) = 0.0417]
completeness to theta = 28.70°	100.0%	100.0%
max. and min. transmission	0.9623 and 0.9180	0.9615 and 0.9075
data/restraints/parameters	17 523/131/913	5908/1360/863
goodness-of-fit on F^2	1.066	1.120
final R indices [$I > 2\sigma(I)$]	R1 = 0.0485, wR2 = 0.1199	R1 = 0.0983, wR2 = 0.2184
R indices (all data)	R1 = 0.0767, wR2 = 0.1332	R1 = 0.1112, wR2 = 0.2280
largest diff. peak and hole	1.613 and -0.375 eÅ^{-3}	1.447 and -1.044 eÅ^{-3}

[a] In each case crystal data were recorded at 100 K with $\lambda = 0.710\ 73$ Å; the refinement method was full-matrix least-squares on F^2, and the absorption correction was semiempirical from equivalents.

rings. The λ_{max} value for **12** is 384 nm (in CH$_2$Cl$_2$), 20 nm lower than λ_{max} for the all five-membered ring trimer in CH$_2$Cl$_2$ (404 nm, vide infra and Table 3). Although more studies of other oligoenes that contain six-membered ring "errors" are necessary, it would appear that the presence of one six-membered ring leads to a significant decrease in λ_{max}.

"Dimeric" and "Trimeric" Aldehydes and Reactions That Employ Them. We envisioned that the same methodology used to prepare aldehydes **2a** and **2b** might be employed to synthesize longer chain analogues. In order to test this hypothesis, aldehyde **2b** was treated with monodeprotonated diisopropyldipropargyl-malonate (eq 9). The resulting propargylic alcohol (**13**) proved,

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **7** and **17**

	7		17	
Mo(1)−N(1)	1.718(3)	Mo(1)−N(1)	1.697(7)	
Mo(1)−C(1)	1.911(3)	Mo(1)−C(1)	1.925(8)	
Mo(1)−O(1)	1.918(2)	Mo(1)−O(1)	1.938(5)	
Mo(1)−O(2)	1.923(2)	Mo(1)−O(2)	1.927(7)	
Mo(2)−N(2)	1.725(3)	Mo(1)−O(1E)	2.388(11)	
Mo(2)−C(2)	1.914(3)	C(1)−C(2)	1.411(11)	
Mo(2)−O(4)	1.927(2)	C(2)−C(6)	1.354(11)	
Mo(2)−O(3)	1.940(2)	C(6)−C(7)	1.428(11)	
C(1)−C(3)	1.434(4)	C(7)−C(7A)	1.343(15)	
C(2)−C(4)	1.421(4)	N(1)−Mo(1)−C(1)	98.6(3)	
C(3)−C(4)	1.378(4)	N(1)−Mo(1)−O(1)	113.1(3)	
N(1)−Mo(1)−C(1)	98.98(13)	N(1)−Mo(1)−O(2)	119.2(3)	
O(1)−Mo(1)−O(2)	115.38(10)	O(1E)−Mo(1)−C(1)	167.7(5)	
Mo(1)−N(1)−C(11)	177.4(2)	O(1E)−Mo(1)−N(1)	93.4(5)	
Mo(1)−C(1)−C(3)	138.2(2)	O(1)−Mo(1)−O(2)	120.9(3)	
N(2)−Mo(2)−C(2)	98.51(13)	Mo(1)−N(1)−C(14)	171.8(6)	
O(3)−Mo(2)−O(4)	116.98(10)	Mo(1)−C(1)−C(2)	137.3(6)	
Mo(2)−N(2)−C(21)	176.7(2)	C(1)−C(2)−C(6)	127.1(7)	
Mo(2)−C(2)−C(4)	139.7(2)	C(2)−C(6)−C(7)	127.0(7)	
C(4)−C(3)−C(1)	126.4(3)	C(6)−C(7)−C(7A)	125.5(9)	
C(3)−C(4)−C(2)	125.7(3)			

well as a high catalyst loading was necessary. For example, with a low catalyst loading (2%) the starting material was consumed quickly, but only traces of the desired product could be isolated. Dimeric aldehyde **2b₂** is bright yellow, is stable in air, and can be stored for long periods. The reaction sequence shown in eqs 11 and 12 produced the "trimeric" aldehyde **2b₃** as a deep yellow solid. Like **2b₂**, aldehyde **2b₃** crystallizes

$$(11)$$

$$(12)$$

readily in pure form after filtering the reaction mixture through a silica gel plug and evaporating the solvent. This methodology has not yet been employed to prepare longer polyenals.

With **8**, **2b₂**, and **2b₃** in hand, the stage was set to synthesize longer odd-numbered analogues of **3b₃**. Reactions between **8** and **2b₂** and **2b₃** in methylene chloride yielded the "pentameric" undecaene (eq 13) and the "heptameric" pentadecaene (eq 14), respectively, in good yields as red microcrystalline solids. The
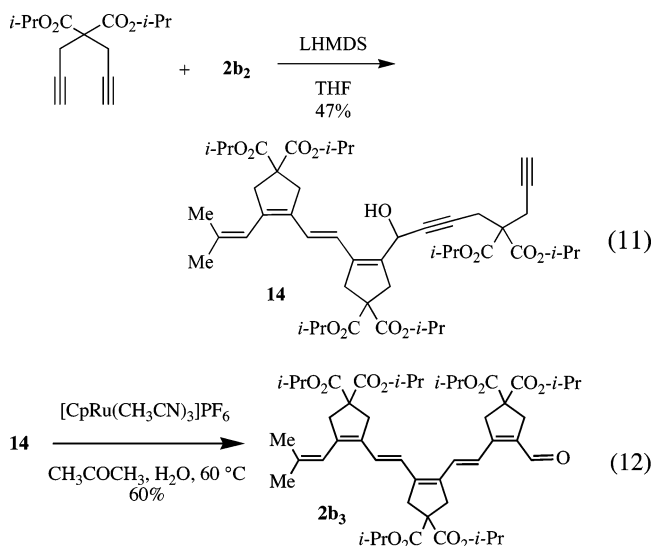

$$(8)$$

not unexpectedly, to be sensitive to traces of acid. For example, when **13** was dissolved in CDCl₃, which contained traces of HCl, clean formation of the cumulene through loss of water was observed over the course of 1 h. Nevertheless **13** could be cyclized to the "dimeric" aldehyde **2b₂** (eq 10). The reaction
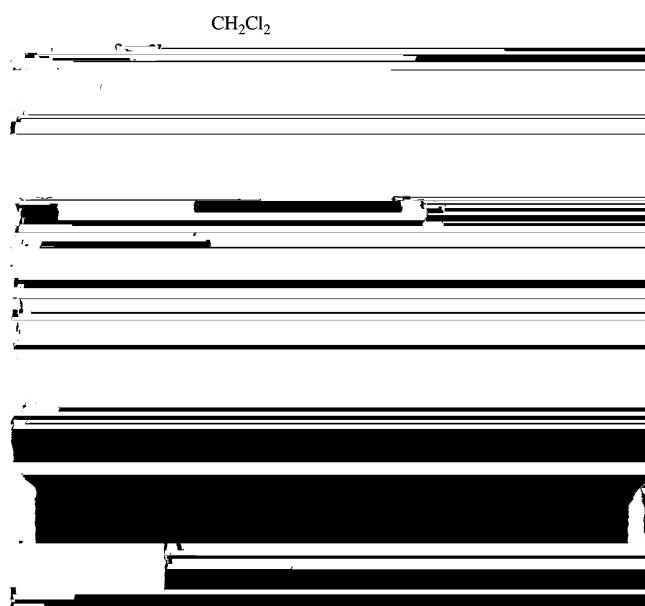

$$(10)$$
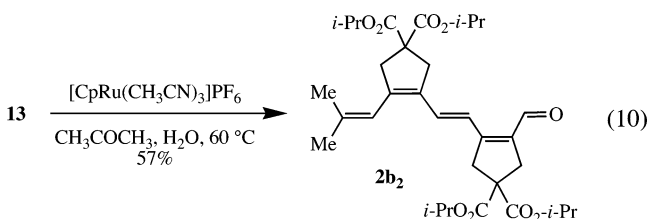
conditions for this cyclization had to be chosen carefully. It was found that a 9:1 mixture of acetone and water at reflux as

reactions are relatively rapid (minutes), and the products can be precipitated readily from solution in high purity. They are

relatively insoluble in pentane, ether, or benzene but soluble in dichloromethane. Unfortunately, the oligoenes tend to form microcrystalline fibrous solids that resemble cotton candy. So far we have not been able to prepare single crystals that are suitable for X-ray studies.

Reactions of the type shown in eqs 5, 13, and 14 yield oligoenes that contain an odd number of repeat units. Even-membered oligoenes are not accessible directly in pure form using this method. (Of course, mixtures that contain even-membered oligoenes could be generated in reactions between **8** and a mixture of **2b₂** and **2b₃**, for example.) We envisioned that reaction of a complex related to **1a**

Extrapolation of N to infinity yields a limit of $E(0-0) \approx 15\ 500$ cm^{-1} ($\lambda = 650$ nm) in dichloromethane.

Synthesis of a Dimeric Bimetallic Species and Its X-ray Structure. The key to the stoichiometric synthesis of symmetric oligoenes of some significant length is the bimetallic species

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parameters as well as rigid bond restraints for anisotropic displacement parameters were applied to all solvent atoms. Nevertheless, mathematical correlation between coordinates and anisotropic displacement parameters of the disordered atoms gives rise to unusually shaped thermal ellipsoids for some of the pentane atoms. This should not affect the accuracy of the structure of the main molecule, and the low residual values of the refinement attest to the overall high quality of the structure of **7**. The hydrogen atoms bound to C(1) and C(2) were taken from the difference Fourier synthesis and refined semifreely with the help of distance restraints, while constraining their U-values to 1.2 times the U_{eq} value of the atom to which they are bound. Further details of the data quality and a summary of the residual values of the refinements are listed in Table 1.

Mo(CH[5](CO₂-*i*-Pr)₂)(NAr)(OR_F6)₂ (1b). Triene **15** (1.41 g, 4.60 mmol) was dissolved in pentane (5 mL), and molecular sieves (4 Å) were added. After 2 h, the solution was decanted and added to a solution of Mo(CHCMe₃)(NAr)(OR_F6)₂ (3.24 g, 4.60 mmol) in pentane (30 mL), and the mixture was stirred for 1 h. The orange precipitate was collected on a frit and washed with cold pentane; the yield of **1b** was 3.03 g (3.27 mmol, 71%): ¹H NMR (500 MHz, CD₂Cl₂) ä 12.80 (s, 1H, J_{CH} = 130 Hz, Mo=C*H*R), 7.27 (t, 1H, J = 7.5 Hz, *p*-Ar), 7.18 (d, 2H, J = 7.5 Hz, *m*-Ar), 5.97 (s, 1H, C*H*=CMe₂), 4.86 (sept, 2H, J = 6.5 Hz, OC*H*Me₂), 3.70 (s, 2H, C*H₂*), 3.53 (sept, 2H, J = 6.3 Hz, C*H*Me₂), 3.18 (s, 2H, C*H₂*), 1.96 (s, 3H, Me), 1.91 (s, 3H, Me), 1.43 (s, 6H, C(CF₃)₂*Me*), 1.20 (d, 12H, J = 6.5 Hz, CH*Me₂*), 0.92 (d, 6H, J = 6.3 Hz, OCH*Me₂*), 1.00 (d, 6H, J = 6.3 Hz, OCH*Me₂*); ¹³C NMR (125 MHz, CD₂Cl₂) ä 258.9, 171.4, 154.7, 148.6, 143.9, 140.1, 130.1, 126.8, 124.4 (q, J_{CF} = 288 Hz, *C*F₃), 124.1 (q, J_{CF} = 288 Hz, *C*F₃), 123.8, 119.2, 81.3 (quin, J = 29 Hz, *C*(CF₃)₂Me), 69.4, 58.0, 45.4, 43.4, 29.1, 28.1, 23.9, 21.7, 20.3, 19.4; ¹⁹F NMR (282 MHz, C₆D₆) ä −77.79. Anal. Calcd for C₃₈H₄₉NF₁₂MoO₆: C, 48.57; H, 5.26; N, 1.49. Found: C, 48.95; H, 5.47; N, 1.49.

[Mo(NAr)(OR_F6)₂]CH[5](CO₂Et)₂CH[Mo(NAr)(OR_F6)₂] (7). Triene **6a** (35.0 mg, 0.132 mmol) was dissolved in pentane (5 mL), and the solution was treated with molecular sieves (4 Å) for 15 min. Pentane (5 mL) was then used to dissolve Mo(NAr)(CHCMe₃)(OR_F6)₂ (186 mg, 0.265 mmol). The solution of **6a** was slowly added to the Mo solution, and the mixture was stirred for 4 h. The solution was then concentrated and stored at −40 °C to yield two crops of crystals (124 mg, 82.0 í mol, 62%). Crystals suitable for X-ray studies were selected from this batch: ¹H NMR (500 MHz, CD₂Cl₂) ä 12.65 (s, 2H, J_{CH} = 125 Hz, Mo=C*H*R), 7.28 (t, 2H, J = 7.5 Hz, *p*-Ar), 7.17 (d, 4H, J = 7.5 Hz, *m*-Ar), 3.84 (q, 4H, J = 7.0 Hz, OC*H₂*), 3.60 (s, 4H, C*H₂*), 3.47 (sept, 4H, J = 7.0 Hz, C*H*Me₂), 1.39 (s, 12H, C(CF₃)₂*Me*), 1.17 (d, 24H, J = 7.0 Hz, CH*Me₂*), 0.93 (t, 6H, J = 7.0 Hz, OCH₂C*H₃*); ¹⁹F NMR (282 MHz, C₆D₆) ä −78.19 (br s), −78.36 (br s).

[Mo(NAr′)(OR_F6)₂]CH[5](CO₂-*i*-Pr)₂CH[Mo(NAr′)(OR_F6)₂] (8). A 50 mL round-bottom flask was charged with Mo(NAr′)(CHCMe₂Ph)-(OR_F6)₂ (609 mg, 0.858 mmol), which was subsequently dissolved in diethyl ether (12 mL). Triene **6b** (125 mg, 0.429 mmol) was dissolved in diethyl ether (8 mL), and the solution was stood over molecular sieves (4 Å) for 30 min. It was then added slowly to the complex solution, and the mixture was stirred for 18 h. The solvent was removed in vacuo, and the residue was redissolved in pentane/diethyl ether (15: 0.7 mL). Storage at −40 °C yielded pure crystalline material (2 crops, 494 mg, 0.348 mmol, 81%): ¹H NMR (500 MHz, CD₂Cl₂) ä 12.66 (s, 2H, J_{CH} = 128 Hz, Mo=C*H*R), 7.13 (m, 6H, Ar), 4.78 (septet, 2H, J = 6.5 Hz, OC*H*Me₂), 3.62 (s, 4H, C*H₂*), 2.39 (s, 12H, Ar*Me*), 1.37 (s, 12H, C(CF₃)₂*Me*) 0.96 (d, 12H, J = 6.5 Hz, CH*Me₂*); ¹³C NMR (125 MHz, CD₂Cl₂) ä 275.3, 170.9, 157.5, 138.1, 133.1, 129.8, 128.5, 124.1 (q, J_{CF} = 286 Hz, *C*F₃), 123.9 (q, J_{CF} = 288 Hz, *C*F₃

1.54 (s, 6H, Me), 0.98 (m, 24H, OCH*Me*$_2$); ^{13}C NMR (125 MHz, C$_6$D$_6$) ä 171.9, 137.1, 136.9, 134.5, 124.5, 120.4, 69.1, 58.7, 45.7, 41.0, 27.6, 21.8 (m), 20.8. IR (CDCl$_3$) cm^{-1} 3141 (w), 2984, 2907, 1724 (s), 1446, 1368, 1259 (s), 1192, 1095, 1074, 1011. HRMS (EI, [M]$^+$). Calcd for

solution was stirred for 24 h at room temperature during which time the color lightened to yellow-brown. The solvent volume was reduced in vacuo to ~5 mL, and 10 mL of pentane was added. The solution was loaded onto a short silica gel column and eluted with 2:1 hexanes/ethyl acetate. The product fractions (R_f = 0.45) were pooled, and the solvent was removed in vacuo yielding 0.0500 g (80%) of a bright yellow film. The compound exists as a 2:1 mixture of isomers as determined by NMR: ^{1}H NMR (500 MHz, CDCl$_3$) *Major isomer δ* 6.61 (s, 1H), 6.56 (d, 1H, J = 16.0 Hz, CH=CH), 6.25 (d, 1H, J = 16.0 Hz, CH=CH), 6.02 (s, 1H), 5.97 (s, 1H), 5.84 (s, 1H), 4.20 (m, 12H, OCH_2), 3.38 (s, 2H, CH_2), 3.34 (s, 2H, CH_2), 3.23 (s, 2H, CH_2), 3.20 (s, 2H, CH_2), 2.88 (s, 2H, CH_2), 2.86 (s, 2H, CH_2), 1.87 (s, 3H, Me), 1.82 (s, 3H, Me), 1.81 (s, 3H, Me), 1.73 (s, 3H, Me), 1.25 (m, 18H, OCH$_2$CH_3); *Minor isomer δ* 6.51 (d, 1H, J = 16.0 Hz, CH=CH), 6.19 (d, 1H, J = 16.0 Hz, CH=CH), 6.15 (s, 1H), 6.08 (s, 1H), 6.01 (s, 1H), 5.84 (s, 1H), 4.20 (m, 12H, OCH_2), 3.40 (s, 2H, CH_2), 3.32 (s, 2H, CH_2), 3.20 (s, 2H, CH_2), 3.18 (s, 2H, CH_2), 3.07 (s, 2H, CH_2), 2.85 (s, 2H, CH_2), 1.87 (s, 3H, Me), 1.83 (s, 3H, Me), 1.80 (s, 3H, Me), 1.71 (s, 3H, Me), 1.25 (m, 18H, OCH$_2$CH_3); ^{13}C NMR (125 MHz, CDCl$_3$) *Both isomers δ* 172.3, 172.2, 172.2, 171.2, 171.1, 138.4, 137.9, 137.6, 137.5, 137.2, 137.1, 136.4, 136.1, 136.0, 134.4, 133.8, 133.7, 133.2, 132.8, 132.7, 132.4, 131.9, 131.4, 130.8, 126.8, 125.4, 123.3, 122.5, 121.8, 120.1, 120.0, 119.5, 61.9, 61.8, 61.8, 61.7, 59.0, 58.9, 58.0, 57.9, 54.4, 54.2, 44.7, 44.6, 43.7, 43.4, 42.7, 40.3, 40.2, 38.5, 32.3, 30.8, 30.4, 27.8, 27.4, 20.7, 20.6, 20.5, 14.3, 14.2, 14.2, 14.1. HRMS (ESI, [MH]$^+$): Calcd for C$_{45}$H$_{61}$O$_{12}$: 793.4158. Found: 793.4170. UV$-$vis: i_{max} = 384 nm (CH$_2$Cl$_2$).

Supporting Information Available: Experimental details for all organic compounds except the polyene oligomers. Fully labeled thermal ellipsoid drawings for **7** and **17**. Data for the structures are available to the public at http://www.reciprocal-net.org (numbers 05149 for **17** and 05196 for **7**). This material is available free of charge via the Internet at http://pubs.acs.org.

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