Supporting Information

Functionalizing Molecular Wires: A Tunable Class of α,ω-diphenyl-μ,ν-dicyano-oligoenes

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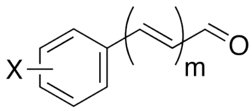
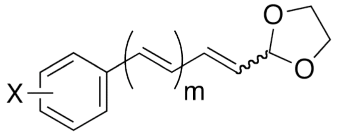
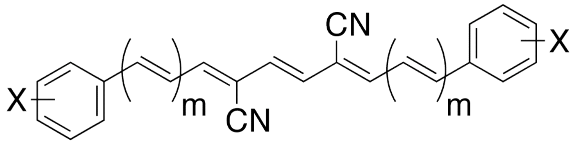
I. List of Compounds:



X	m	Molecule
H	2	**1a**
H	3	**1b**
H	4	**1c**
H	5	**1d**
4-SMe	1	**2a**
4-SMe	2	**2b**
4-SMe	3	**2c4**
4-SMe	4	**2d**
4-SC_4H_8	0	**3a**
4-SC_4H_8	1	**3b**
4-SC_4H_8	2	**3c**
4-SC_4H_8	3	**3d**
4-SC_4H_8	4	**3e**
4-SC_5H_{10}	0	**4a**
4-SC_5H_{10}	1	**4b**
4-SC_5H_{10}	2	**4c**
4-SC_5H_{10}	3	**4d**
4-SC_5H_{10}	4	**4e**
4-SC_5H_{10}	5	**4f**
4-Me_2N	2	**5a**
4-Ph_2N	1	**6a**
4-Br	1	**7a**
4-Br	2	**7b**
4-Br	3	**7c**
4-CO_2H	0	**8a**
4-CO_2H	1	**8b**
4-CO_2H	2	**8c**
4-CO_2Et	0	**9a**
4-CO_2Et	1	**9b**
4-CO_2Et	2	**9c**
3,5-OC_6H_{13}	0	**10a**
3,5-OC_6H_{13}	1	**10b**
3,5-OC_6H_{13}	2	**10c**
3,5-$OC_{10}H_{21}$	0	**11a**
3,5-$OC_{10}H_{21}$	1	**11b**
3,5-$OC_{10}H_{21}$	2	**11c**
3,5-$OC_{14}H_{29}$	0	**12a**
3,5-$OC_{14}H_{29}$	1	**12b**
4-$C\equiv C\text{-}C_6H_{13}$	0	**13a**
4-$C\equiv C\text{-}C_6H_{13}$	1	**13b**
4-$C\equiv C\text{-}C_6H_{13}$	2	**13c**
4-CN	1	**14a**



X	m	E/Z	Molecule
H	2	*E*	***E*-1e**
H	2	*Z*	***Z*-1e**
Br	1	*E*	***E*-7d**
Br	1	*Z*	***Z*-7d**
Br	2	*E*	***E*-7e**
Br	2	*Z*	***Z*-7e**



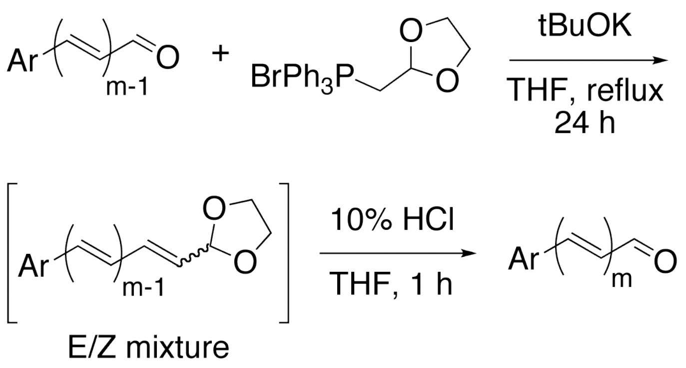
DPDCn-X

X	m	Total n	Molecule
H	0	3	**DPDC3**
H	1	5	**DPDC5**
H	2	7	**DPDC7**
H	3	9	**DPDC9**
H	4	11	**DPDC11**
H	5	13	**DPDC13**
4-SMe	0	3	**DPDC3-SMe**
4-SMe	1	5	**DPDC5-SMe**
4-SMe	2	7	**DPDC7-SMe**
4-SMe	3	9	**DPDC9-SMe**
4-SMe	4	11	**DPDC11-SMe**
4-SC$_4$H$_8$	0	3	**DPDC3-SC$_4$H$_8$**
4-SC$_4$H$_8$	1	5	**DPDC5-SC$_4$H$_8$**
4-SC$_4$H$_8$	2	7	**DPDC7-SC$_4$H$_8$**
4-SC$_4$H$_8$	3	9	**DPDC9-SC$_4$H$_8$**
4-SC$_4$H$_8$	4	11	**DPDC11-SC$_4$H$_8$**
4-SC$_5$H$_{10}$	0	3	**DPDC3-SC$_5$H$_{10}$**
4-SC$_5$H$_{10}$	1	5	**DPDC5-SC$_5$H$_{10}$**
4-SC$_5$H$_{10}$	2	7	**DPDC7-SC$_5$H$_{10}$**
4-SC$_5$H$_{10}$	3	9	**DPDC9-SC$_5$H$_{10}$**
4-SC$_5$H$_{10}$	4	11	**DPDC11-SC$_5$H$_{10}$**
4-SC$_5$H$_{10}$	5	13	**DPDC13-SC$_5$H$_{10}$**
4-Me$_2$N	0	3	**DPDC3-NMe$_2$**
4-Me$_2$N	1	5	**DPDC5-NMe$_2$**
4-Me$_2$N	2	7	**DPDC7-NMe$_2$**
4-Ph$_2$N	0	3	**DPDC3-NPh$_2$**
4-Ph$_2$N	1	5	**DPDC5-NPh$_2$**
4-Br	0	3	**DPDC3-Br**
4-Br	1	5	**DPDC5-Br**
4-Br	2	7	**DPDC7-Br**
4-Br	3	9	**DPDC9-Br**
4-CO$_2$H	0	3	**DPDC3-CO$_2$H**
4-CO$_2$H	1	5	**DPDC5-CO$_2$H**
4-CO$_2$H	2	7	**DPDC7-CO$_2$H**
4-CO$_2$Et	0	3	**DPDC3-CO$_2$Et**
4-CO$_2$Et	1	5	**DPDC5-CO$_2$Et**
4-CO$_2$Et	2	7	**DPDC7-CO$_2$Et**
3,5-OC$_6$H$_{13}$	0	3	**DPDC3-OC$_6$H$_{13}$**
3,5-OC$_6$H$_{13}$	1	5	**DPDC5-OC$_6$H$_{13}$**
3,5-OC$_6$H$_{13}$	2	7	**DPDC7-OC$_6$H$_{13}$**
3,5-OC$_{10}$H$_{21}$	0	3	**DPDC3-OC$_{10}$H$_{21}$**

3,5-$OC_{10}H_{21}$	1	5	**DPDC5-$OC_{10}H_{21}$**
3,5-$OC_{10}H_{21}$	2	7	**DPDC7-$OC_{10}H_{21}$**
3,5-$OC_{14}H_{29}$	0	3	**DPDC3-$OC_{14}H_{29}$**
3,5-$OC_{14}H_{29}$	1	5	**DPDC5-$OC_{14}H_{29}$**
4-$C\equiv C$-C_6H_{13}	0	3	**DPDC3-C_8H_{13}**
4-$C\equiv C$-C_6H_{13}	1	5	**DPDC5-C_8H_{13}**
4-$C\equiv C$-C_6H_{13}	2	7	**DPDC7-C_8H_{13}**
4-CN	0	3	**DPDC3-CN**
4-CN	1	5	**DPDC5-CN**
2-Br	0	3	***ortho*-DPDC3-Br**
3-Br	0	3	***meta*-DPDC3-Br**
2-OMe	0	3	***ortho*-DPDC3-OMe**
3-OMe	0	3	***meta*-DPDC3-OMe**
4-OMe	0	3	**DPDC3-OMe**
3-NO_2	0	3	***meta*-DPDC3-NO_2**
4-NO_2	0	3	**DPDC3-NO_2**
4-NO2	0	5	**DPDC5-NO_2**
4-F	0	5	**DPDC5-NO_2**

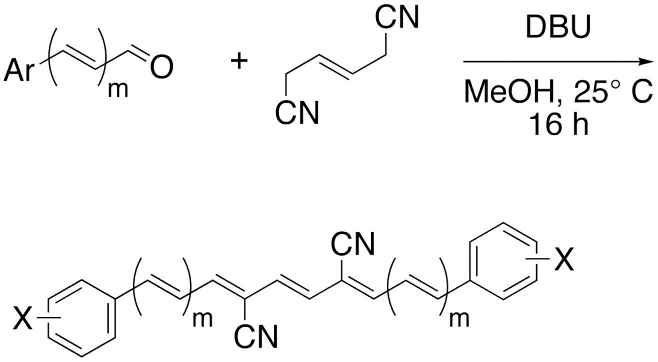
II. Synthetic Details

General Information: (1,3-dioxolan-2-yl)methyl-triphenylphosphonium bromide was purchased from TCI America and stored in a desiccator. Benzaldehyde, 4-bromobenzaldehyde, 3-bromobenzaldehyde, 2-bromobenzaldehyde, 4-methoxybenzaldehyde, 3-methoxybenzaldehyde, 2-methoxybenzaldehyde, 4-(methylthio)-benzaldehyde, 4-(dimethylamino)-benzaldehyde, 4-formal benzoic acid, 4-fluorobenzaldehyde, 4-nitrobenzaldehyde, 3-nitrobenzaldehyde, 4-cyanobenzaldehyde, *trans*-cinnamaldehyde, trans-(4-dimethylamino)cinnamaldehyde and trans-(4-nitro)cinnamaldehyde, 1,4-dicyano-2-butene, 1,2-epoxy-2-methylpropane, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 3,3-dimethylallyl bromide and all other reagents were purchased from Sigma-Aldrich Chemical. Alkoxybenzaldehydes,[1] α,ω-diphenyl-oligoenes (**DPOn**) and α,ω-(4-dimethylamino)phenyl-deca-pentaene[2] (**DPO-NMe$_2$**) were synthesized according to the literature. All reactions were carried out under nitrogen unless otherwise noted. All chromatography was performed on a Teledyne ISCO Combiflash RF using Redisep RF silica columns. ^{1}H and ^{13}C NMRs were recorded on a Bruker DRX300 (300MHz), DRX400 (400MHz) or Bruker DMX500 (500MHz). In general, mass spectrometry for the oligoenes was difficult to interpret. ^{1}H and ^{13}C NMR spectra for the compounds prepared here are contained at the end of the Supporting Information.



General Procedure for Wittig Homologation of Aldehydes: As an example, lithium methoxide (0.149 g, 3.93 mmol, 2.6 eq.) was added to a stirring solution of (1,3-dioxolan-2-yl)methyl-triphenylphosphonium bromide (1.62 g, 3.78 mmol, 2.5 eq.) in 50 mL of anhydrous tetrahydrofuran (THF) in a 100-mL round-bottom flask. The suspension was heated to reflux stirred for 30 minutes, changing color from off-white to light orange/pink. *trans*-cinnamaldehyde (0.200 g, 1.51 mmol, 1.0 eq.) in 20 mL of dry THF solution was added dropwise over 30-60 min. The suspension was refluxed for 24 h. The reaction suspension was then cooled to room temperature, at which point 10% aqueous hydrochloric acid (HCl) was added. Stirring was continued for 1 hour in order to hydrolyze the intermediate acetals (mixture of *E*- and *Z*-stereoisomers) to the all-*trans* configuration. The organic layer was extracted with CH_2Cl_2 (25 mL x3) and the combined fractions were washed with water, sat. aqueous sodium bicarbonate solution and brine, and then dried over $MgSO_4$. Solvent was removed by rotary evaporation and the product was purified via column chromatography using an eluent gradient from 0% to 10% ethyl acetate in hexanes over 25 column volumes. The product, in this case (2*E*,4*E*)-5-phenylpenta-2,4-dienal, was obtained in 92% yield (0.199 g) as a yellow oil. This reaction was typically carried out on 0.200 g of starting aldehyde for quick work up and separation, but can easily be scaled up to multi-gram quantities. We have attempted this reaction on a 5.00 g scale without significant loss in yield (~3.7%).

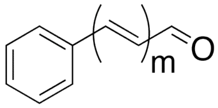
Alternatively, the (*E*)- and (*Z*)-acetals may be isolated by column chromatography. As in the reaction above, *trans*-cinnamaldehyde is reacted with the triphenylphosphonium salt. After refluxing for 24 h the reaction was cooled to room temperature, diluted with water, extracted with CH_2Cl_2 (3x) and dried over $MgSO_4$. The organic solvent was removed by rotary evaporation. The (*E*)- and (*Z*)--diene-acetals were isolated by column chromatography 5% ethyl acetate in hexanes ($Rf_E/Rf_Z = 0.2/0.1$) in 16.6% and 70.8%, respectively. (*Z*)-isomer is produced in 14:3 ratio compared with the (*E*)-isomer. When 10% aq. HCl solution is added to a solution of either stereoisomer or a mixture of isomers only the *E*-enal, the desired product, is obtained (see ^{1}H and ^{13}C NMR for compound **1a**). In the route to most DPDC's we did not isolate the intermediate acetals. In few circumstances it was synthetically necessary to isolate these acetals in order to synthesize the carboxylic acid polyenals for our **DPDCn-CO_2H** series (see **7e** and **7d**).



DPDCn-X

General Procedure for Double Knoevenagel Condensation: The appropriate oligoenal (150 mg) and 1,4-dicyano-2-butene (0.75 eq.) were dissolved in wet methanol (25-50 mL) in a 100-mL round-bottomed flask (anhydrous solvents do not effect isolated yield). In some cases, the aryl-oligoenals were insoluble in methanol and a methanol/tetrahydrofuran mixture was used instead. The flask was sealed with a rubber septum and purged by bubbling nitrogen through the reaction solution for 10 minutes. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 1.0 eq.) were added via syringe and the solution was left stirring for 16 hours, over which the product usually precipitated out. The crude product was filtered off and washed with methanol and then purified either by recrystallization from dichloromethane/methanol or by flash column chromatography using dichloromethane/hexanes (1:1) as eluent. To test whether this procedure was scalable we prepared **DPDC5** on gram quantities without a significant loss in yield (~4%).

Specific Experimentals and Characterization:



1a; m = 2
1b; m = 3
1c; m = 4
1d; m = 5

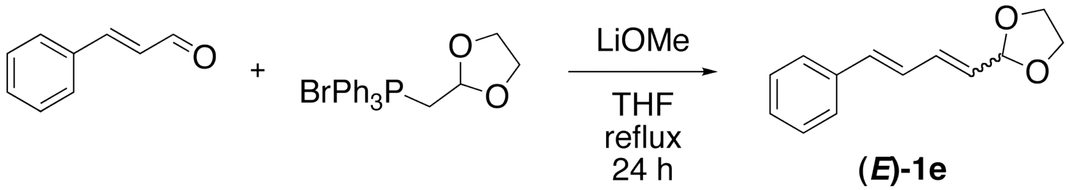
(2E,4E)-5-phenylpenta-2,4-dienal (**1a**; m = 2): General Wittig homologation procedure. The product was prepared from *trans*-cinnamaldehyde and isolated as a yellow oil in 92.0% yield. This compound is known and agrees with spectroscopic data in literature.[3] ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.63 (d, *J* = 8.1 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.34 (m, 4H), 7.07-7.10 (m, 2H), 6.30 (dd, *J* = 7.9 Hz, 15.2 Hz, 1H); ^{13}C NMR (400 MHz, CD_2Cl_2): δ 194.1, 152.6, 142.9, 136.0, 132.0, 130.1, 129.4, 128.0, 126.6.

(2E,4E,6E)-7-phenylhepta-2,4,6-trienal (**1b**; m = 3): General Wittig homologation procedure. The product was prepared from **1a** and isolated as a dark yellow solid in 88.0% yield. This compound is known and agrees with spectrocopic data in literature.[4,5] ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.62 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.40-7.28 (m, 3H), 7.23 (dd, *J* = 11.6 Hz, 15.2 Hz, 1H), 6.96-6.86 (m, 3H), 6.61 (dd, *J* = 11.2 Hz, 14.0 Hz, 1H), 6.22 (dd, *J* = 8.0 Hz, 15.2 Hz, 1H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 193.45, 151.67, 142.71, 138.34, 136.36, 131.23, 130.15, 128.85, 128.83, 127.72, 127.02.

(2E,4E,6E,8E)-9-phenylnona-2,4,6,8-tetraenal (**1c**; m = 4): General Wittig homologation procedure. The product was prepared from **1b** and isolated as an orange solid in 70.0% yield. This compound is known and agrees with spectroscopic data in literature.[4,5] ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.59 (d, *J* = 8.1 Hz, 1H), 7.45 (d, *J* = 7.2 Hz, 2H), 7.37-7.24 (m, 3H), 7.17 (dd, *J* = 11.4 Hz, 15.0 Hz, 1H), 6.90 (dd, *J* = 10.8 Hz, 15.3 Hz, 1H), 6.82-6.42 (m, 5H), 6.19 (dd, *J* = 8.1 Hz, 15.0 Hz, 1H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 193.45, 151.72, 142.61, 138.93, 136.76, 136.06, 131.86, 131.02, 129.98, 128.78, 128.36, 128.35, 126.77.

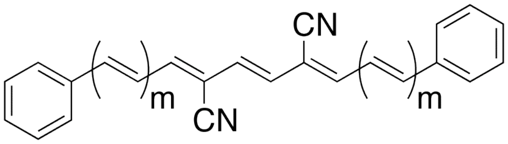
(2E,4E,6E,8E,10E)-11-phenylundeca-2,4,6,8,10-pentaenal (**1d**; m = 5): General Wittig homologation procedure. The product was prepared from **1c** and isolated as a dark orange

solid in 55.0% yield. This compound is known and agrees with spectroscopic data in literature.[4,6] ^{1}H NMR (300 MHz, CDCl$_3$): δ 9.61 (d, *J* = 7.2 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 8.1 Hz, 2H), 7.27 (t, *J* = 6.5 Hz, 1H), 7.18 (dd, *J* = 11.2 Hz, 15.1 Hz, 1H), 6.90 (dd, *J* = 10.8 Hz, 15.4 Hz, 1H), 6.77 (dd, *J* = 11.4 Hz, 14.6 Hz, 1H), 6.68 (d, *J* = 15.6 Hz, 1H), 6.64-6.30 (m, 5H), 6.18 (dd, *J* = 8.1 Hz, 15.0 Hz, 1H); ^{13}C NMR (300 MHz, CDCl$_3$): δ 193.44, 151.72, 142.67, 138.83, 137.00, 136.76, 134.78, 132.63, 131.75, 130.92, 129.93, 128.73, 128.71, 128.05, 126.61.



(*E*)-1e
(*Z*)-1e

2-((1E,3E)-4-phenylbuta-1,3-dienyl)-1,3-dioxolane (***E*-1e**) and *2-((1Z,3E)-4-phenylbuta-1,3-dienyl)-1,3-dioxolane* (***Z*-1e**): Using the modified general Wittig homologation procedure outlined above (pp. S6-S7) The (*E*)- and (*Z*)-products were prepared from *trans*-cinnamaldehyde and isolated by column chromatography 5% ethyl acetate in hexanes (Rf_E/Rf_Z = 0.2/0.1) in 16.6% and 70.8% yield, respectively. The (*Z*)-isomer is selectively formed in a 14:3 ratio compared with the (*E*)-isomer. ***E*-1e** was isolated as a pale yellow oil in 16.6% yield. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.41 (d, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 6.79 (dd, *J* = 11.6 Hz, 15.2 Hz, 1H), 6.62 (d, *J* = 15.7 Hz, 1H), 6.52 (dd, *J* = 15.5 Hz, 10.6 Hz, 1H), 5.75 (dd, *J* = 15.5 Hz, 4.9 Hz, 1H), 4.90 (dd, *J* = 4.9 Hz, 0.7 Hz, 1H), 3.35 (s, 4H); ^{13}C NMR (500 MHz, CDCl$_3$): δ 137.0, 134.7, 133.9, 129.4, 128.6, 127.8, 127.7, 126.5, 102.6, 52.6. ***Z*-1e** was isolated as a pale yellow oil in 70.8% yield. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.42 (d, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.14 (ddd, *J* = 15.5 Hz, 11.3 Hz, 0.9 Hz, 1H), 6.60 (d, *J* = 15.6 Hz, 1H), 6.34 (t, *J* = 11.2 Hz, 1H), 5.48 (dd, *J* = 11.1 Hz, 5.9 Hz, 1H), 5.32 (dd, *J* = 5.9 Hz, 1.2 Hz, 1H), 3.34 (s, 4H); ^{13}C NMR (500 MHz, CDCl$_3$): δ 136.9, 135.5, 132.5, 128.7, 128.1, 127.4, 126.7, 123.9, 99.8, 52.2.



DPDCn; m = 0, 1, 2, 3, 4, 5

(1Z,3E,5Z)-2,5-dicyano-1,6-diphenyl-hexa-1,3,5-triene (**DPDC3**; m = 0): General double Knoevenagel condensation procedure. The product was prepared from benzaldehyde and isolated as a yellow crystalline solid in 55.0% yield. ^{1}H NMR (300 MHz, $C_2D_2Cl_4$): δ 7.87-7.84 (m, 4H), 7.47 (m, 6H), 7.22 (s, 2H), 6.87 (s, 2H); ^{13}C NMR (300 MHz, 350 K, $C_2D_2Cl_4$): δ 145.60, 133.12, 131.07, 130.08, 129.29, 129.02, 116.02, 109.31.

(1E,3Z,5E,7Z,9E)-4,7-dicyano-1,10-diphenyl-deca-1,3,5,7,9-pentaene (**DPDC5**; m = 1): General double Knoevenagel condensation procedure. The product was prepared from *trans*-cinnamaldehyde and isolated as an orange crystalline solid in 60.1% yield. ^{1}H NMR (300 MHz, $C_2D_2Cl_4$): δ 7.59 (d, J = 6.6 Hz, 4H), 7.44-7.28 (m, 8H), 7.08-7.01 (m, 4H), 6.76 (s, 2H); ^{13}C NMR (300 MHz, 350 K, $C_2D_2Cl_4$): δ 145.0, 142.0, 135.6, 129.7, 129.0, 128.8, 127.5, 124.7, 114.8, 111.9.

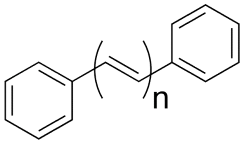
(1E,3E,5Z,7E,9Z,11E,13E)-6,9-dicyano-1,14-diphenyl-tetradeca-1,3,5,7,9,11,13-heptaene (**DPDC7**; m = 2): General double Knoevenagel condensation procedure was run at 55° C. The product was prepared from **1a** and isolated as a red solid in 53.8% yield. ^{1}H NMR (400 MHz, 350 K, DMSO-d_6): δ 7.59 (d, J = 7.6 Hz, 4H), 7.44-7.30 (m, 8H), 7.24 (dd, J = 10.8 Hz, 15.6 Hz, 2H), 7.04-6.95 (m, 4H), 6.84 (dd, J = 11.6 Hz, 14.0 Hz, 2H), 6.75 (s, 2H); ^{13}C NMR (300 MHz, 370 K, DMSO-d_6): δ 146.22, 143.44, 138.76, 137.06, 129.23, 129.18, 129.16, 129.13, 127.59, 115.49, 111.03.

(1E,3E,5E,7Z,9E,11Z,13E,15E,17E)-8,11-dicyano-1,18-diphenyl-octadeca-1,3,5,7,9,11,13,15,17-nonaene (**DPDC9**; m = 3): General double Knoevenagel condensation procedure was run at 55° C. The product was prepared from **1b** and isolated as a dark purple solid in 45.4% yield. ^{1}H NMR (400 MHz, 350 K, DMSO-d_6): δ 7.53 (d, J = 7.6 Hz, 4H), 7.39-7.27 (m, 8H), 7.10-6.68 (m, 14H); ^{13}C NMR (300 MHz, 380 K,

DMSO-d_6): δ 146.25, 143.50, 140.26, 140.00, 137.79, 136.63, 133.42, 129.81, 129.53, 129.27, 128.98, 127.58, 115.86, 111.27.

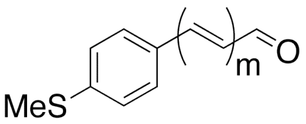
(1E,3E,5E,7E,9Z,11E,13Z,15E,17E,19E,21E)-10,13-dicyano-1,22-diphenyl-docosa-1,3,5,7,9,11,13,15,17,19,21-undecaene (**DPDC11**; m = 4): General double Knoevenagel condensation procedure was run at 55° C. The product was prepared from **1c** and isolated as a lustrous dark purple-black solid in 40.4% yield. ^{1}H NMR (400 MHz, 350 K, $C_2H_2Cl_4$): δ 7.47 (d, J = 7.6 Hz, 4H), 7.37 (t, J = 7.2 Hz, 4H), 7.28 (t, J = 7.2 Hz, 2H), 6.95-6.47 (m, 20H); ^{13}C NMR (400 MHz, 350 K, $C_2D_2Cl_4$): δ 144.0, 141.6, 136.6, 136.4, 134.4, 132.3, 131.7, 128.6, 128.4, 128.2, 127.5, 126.1; due to insolubility four carbon signals were not observed (see crystal structure in supporting information).

(1E,3E,5E,7E,9E,11Z,13E,15Z,17E,19E,21E,23E,25E)-12,15-dicyano-1,26-diphenyl-hexacosa-1,3,5,7,9,11,13,15,17,19,21,23,25-tridecaene (**DPDC13**; m = 5): General double Knoevenagel condensation procedure was run at 55° C. The product was prepared from **1d** and isolated as a lustrous dark black solid in 10.0% yield; ^{1}H and ^{13}H NMR data unavailable due to insolubility (see crystal structure in supporting information).



DPOn; n = 3, 5, 7

(1E,3E,5E)-1,6-diphenyl-hexa-1,3,5-triene (**DPO3**; n = 3), *(1E,3E,5E,7E,9E)-1,10-diphenyl-deca-1,3,5,7,9-pentaene* (**DPO5**; n = 5), and *(1E,3E,5E,7E,9E,11E,13E)-1,14-diphenyl-tetradeca-1,3,5,7,9,11,13-heptaene* (**DPO7**; n = 7) were prepared according to the procedure reported by Spangler and coworkers.[2] Longer **DPOn** molecules, where n > 7, were insoluble and difficult to characterize.



2a; m = 1
2b; m = 2
2c; m = 3
2d; m = 4

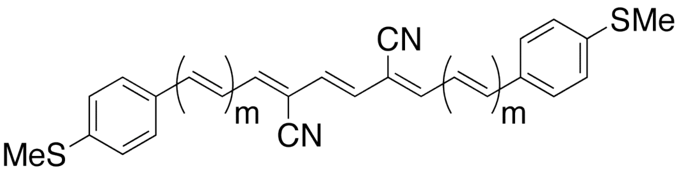
trans-4-(methylthio)cinnamaldehyde (**2a**; m = 1): General Wittig homologation procedure. The product was prepared from (4-methylthio)benzaldehyde and isolated as a pale yellow oil in 96.0% yield. The molecule is known, however specific characterizations have not been reported.**Error! Bookmark not defined.**,7 ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.70 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 16.0 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 6.69 (dd, *J* = 7.6 Hz, 15.6 Hz, 1H), 2.53 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 193.9, 152.2, 144.0, 130.8, 129.2, 128.0, 126.3, 15.4.

(2E,4E)-5-(4-(methylthio)phenyl)penta-2,4-dienal (**2b**; m = 2): General Wittig homologation procedure. The product was prepared from **2a** and isolated as a yellow solid in 99.0% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.62 (d, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.26 (m, 3H), 6.95 (m, 2H), 6.27 (dd, *J* = 8.1 Hz, 15.0 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 193.8, 152.1, 143.2, 140.3, 138.1, 131.4, 130.2, 127.7, 127.4, 126.8, 15.8.

(2E,4E,6E)-7-(4-(methylthio)phenyl)hepta-2,4,6-trienal (**2c**; m = 3): General Wittig homologation procedure. The product was prepared from **2b** and isolated as an orange solid in 73.0% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.60 (d, *J* = 8.1 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.19 (m, 3H), 6.83 (m, 3H), 6.55 (dd, *J* = 11.1 Hz, 15.3 Hz, 1H), 6.19 (dd, *J* = 8.1 Hz, 15.3 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 193.48, 151.78, 142.83, 139.88, 137.78, 133.10, 131.05, 129.85, 127.37, 127.01, 126.35, 15.45.

(2E,4E,6E,8E)-9-(4-(methylthio)phenyl)nona-2,4,6,8-tetraenal (**2d**; m = 4): General Wittig homologation procedure. The product was prepared from **2c** and isolated as an orange-red solid in 70.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.57 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.16 (dd, *J* = 12.0 Hz, 15.9 Hz, 1H), 6.84 (dd, *J* = 10.8 Hz, 15.4 Hz, 1H), 6.76 (dd, *J* = 11.2 Hz, 14.5 Hz, 1H), 6.70-6.58 (m, 2H), 6.47 (m, 2H), 6.17 (dd, *J* = 7.9 Hz, 15.1 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (300 MHz,

$CDCl_3$), 400 MHz: δ 193.9, 152.2, 143.1, 139.4, 135.9, 134.6, 134.0, 132.0, 131.3, 130.3, 128.1, 127.5, 126.9, 16.0.



DPDCn-SMe; m = 0, 1, 2, 3, 4

(1Z,3E,5Z)-2,5-dicyano-1,6-di-(4-(methylthio)phenyl)-hexa-1,3,5-triene (**DPDC3-SMe**; m = 0): General double Knoevenagel condensation procedure. The product was prepared from (4-methylthio)benzaldehyde and isolated as a lemon yellow solid in 70.0% yield. ^{1}H NMR (300 MHz, $C_2D_2Cl_3$): δ 7.78 (d, J = 8.3 Hz, 4H), 7.34 (d, J = 8.3 Hz, 4H), 7.18 (s, 2H), 6.86 (s, 2H), 2.58 (s, 6H); ^{13}C NMR (300 MHz, 350 K, $C_2D_2Cl_4$): δ 144.3, 143.3, 129.9, 129.8, 129.5, 126.1, 116.0, 108.5, 15.0.

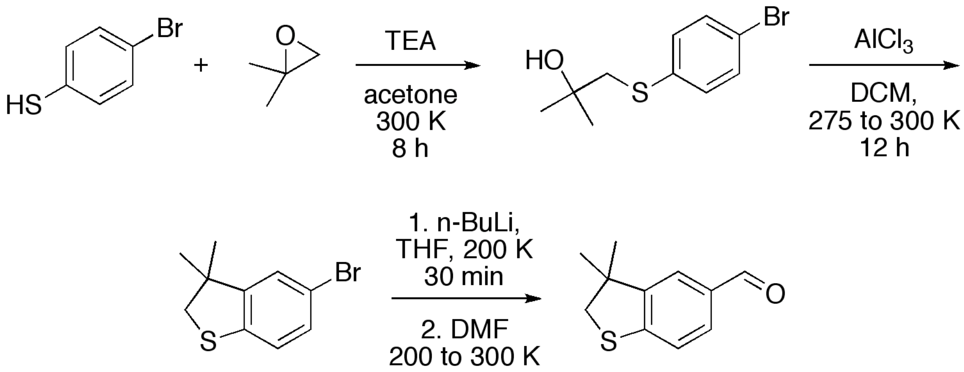
(1E,3Z,5E,7Z,9E)-4,7-dicyano-1,10-di-(4-(methylthio)phenyl)-deca-1,3,5,7,9-pentaene (**DPDC5-SMe**; m = 1): General double Knoevenagel condensation procedure. The product was prepared from **2a** and isolated as a red solid in 45.0% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85 (d, J = 8.4 Hz, 4H), 7.26-7.18 (m, 6H), 7.00 (d, J = 11.4 Hz, 2H), 6.94 (d, J = 15.0 Hz, 2H), 6.68 (s, 2H), 2.52 (s, 6H); ^{13}C NMR (300 MHz, 350 K, $C_2D_2Cl_4$): δ 145.0, 141.4, 141.2, 132.5, 128.8, 127.9, 126.5, 124.1, 115.0, 111.4, 15.3.

(1E,3E,5Z,7E,9Z,11E,13E)-6,9-dicyano-1,14-di-(4-(methylthio)phenyl)-tetradeca-1,3,5,7,9,11,13-heptaene (**DPDC7-SMe**; m = 2): General double Knoevenagel condensation procedure. The product was prepared from **2b** and isolated as a purple crystalline solid in 20.3% yield. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$): δ 7.41 (d, J = 8.4 Hz, 4H), 7.23 (d, J = 8.4 Hz, 4H), 6.99-6.89 (m, 4H), 6.82-6.67 (m, 6H), 6.64 (s, 2H), 2.52 (s, 6H); ^{13}C NMR (300 MHz, 350 K, $C_2D_2Cl_4$): δ 144.21, 142.39, 139.47, 137.47, 132.76, 128.06, 128.5, 127.00, 126.96, 114.76, 110.63, 15.01.

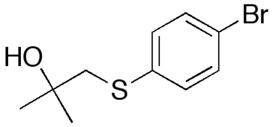
(1E,3E,5E,7Z,9E,11Z,13E,15E,17E)-8,11-dicyano-1,18-di-(4-(methylthio)phenyl)-octadeca-1,3,5,7,9,11,13,15,17-nonaene (**DPDC9-SMe**; m = 3): General Double Knoevenagel Condensation Procedure was carried out at 55° C. The product was prepared from **2c** and isolated as a dark purple-black solid in 40.5% yield. ^{1}H NMR (500

MHz, $C_2D_2Cl_4$): δ 7.40 (d, *J* = 8.5 Hz, 4H), 7.29 (d, *J* = 8.5 Hz, 4H), 7.13-6.34 (m, 16H), 2.54 (s, 6H). ^{13}C NMR could not be obtained due to insolubility.

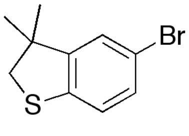
(1E,3E,5E,7E,9Z,11E,13Z,15E,17E,19E,21E)-10,13-dicyano-1,22-di-(4-(methylthio)-phenyl)-docosa-1,3,5,7,9,11,13,15,17,19,21-undecaene (**DPDC11-SMe**; m = 4): General double Knoevenagel condensation procedure. The product was prepared from **2d** and isolated as a lustrous dark black solid in 10.0% yield. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.37 (d, *J* = 8.0 Hz, 4H), 7.22 (d, *J* = 8.0 Hz, 4H), 6.92-6.45 (m, 16H), 6.49 (m, 4H), 2.51 (s, 6H); ^{13}C NMR could not be obtained due to compound insolubility.



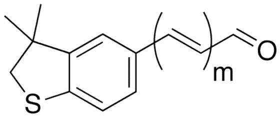
Scheme S1. Synthesis of 3,3-dimethyl-2,3-dihydrobenzo[*b*]thiophene-5-carbaldehyde from 4-bromothiophenol.



4-bromophenylthio 2-methyl-propan-2-ol: 4-bromothiophenol (1.0 g, 5.3 mmol) and 1,2-Epoxy-2-methylpropane (0.76 g, 10.5 mmol) were added to a 100-mL round-bottom flask with magnetic stir bar. The reaction flask was then charged with 50 mL of acetone (from drum) and nitrogen was bubbled through for 20 min. Triethylamine (3 mL) was added to reaction via syringe. The reaction was stirred overnight at room temperature. The organic solvent was removed by rotary evaporation. The product was isolated by column chromatography (20% ethyl acetate in hexanes) and 1.28 g (93%) of clear oil was isolated. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 8.7 Hz, 2H), 3.08 (s, 2H), 2.14 (bs, 1H), 1.30 (s, 6H); ^{13}C NMR (300 MHz, $CDC1_3$): δ 136.8, 132.4, 131.3, 120.4, 71.2, 48.9, 29.1.



5-bromo-3,3-dimethyl-2,3-dihydrobenzo[b]thiophene: A solution of 4-bromophenylthio 2-methyl-propan-2-ol (0.36 g, 1.39 mmol) CH_2Cl_2 was added to a stirring suspension of aluminum chloride (0.20 g, 1.53 mmol) in CH_2Cl_2 cool in an ice bath. The suspension was left to stir overnight while warming to room temperature. Water was added to quench unreacted $AlCl_3$. The organic layer was washed with water and then sat. aqueous sodium chloride solution before drying over $MgSO_4$. The product was isolated by column chromatography (100% hexanes) and 1.90 g (57%) of clear oil was isolated. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23 (dd, *J* = 1.8 Hz, 8.4 Hz, 1H), 7.14 (d, *J* = 1.8 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 3.18 (s, 2H), 1.36 (s, 6H); ^{13}C NMR (300 MHz, $CDC1_3$): δ 150.7, 140.1, 130.6, 126.4, 124.1, 118.2, 47.9, 47.8, 27.6.



3a; m = 1
3b; m = 2
3c; m = 3
3d; m = 4

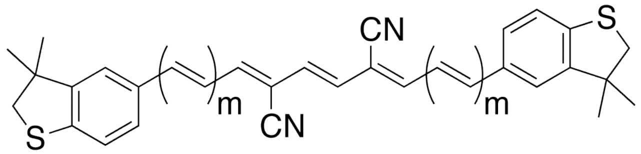
3,3-dimethyl-2,3-dihydrobenzo[b]thiophene-5-carbaldehyde (**3a**; m = 0): A 100-mL round-bottom flask was flame dried and charged with 5-bromo-3,3-dimethyl-2,3-dihydrobenzo[*b*]thiophene (0.310 g, 1.20 mmol) and anhydrous THF (25 mL). The reaction flask was cooled to -78° C in an acetone/dry ice bath for 40 min. 0.9 mL of n-BuLi (1.6 M in hexanes) was dripped into the reaction slowly over 5 minutes. The reaction was allowed to stir at -78° C for 30 min before dry DMF (1 mL) was added dropwise. This reaction was allowed to warm to room temperature overnight. The reaction was then quenched with water, left to stir for 10 min and extracted with ether. The organic layers were combined and washed with sat. sodium chloride solution and then dried over $MgSO_4$. Product was isolated by column chromatography to yield 0.203 g (94 %) of a colorless oil. NOTE: yields varied. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.88 (s, 1H), 7.62 (dd, *J* = 1.8 Hz, 8.1 Hz, 1H), 7.55 (d, *J* = 1.8 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 1H), 3.24 (s, 2H), 1.41 (s, 6H); ^{13}C NMR (300 MHz, $CDC1_3$): δ 191.6, 150.5, 149.6, 134.1, 131.1, 123.0, 122.9, 47.8, 47.3, 27.9.

(E)-3-(3,3-dimethyl-2,3-dihydrobenzo[b]thiophen-5-yl)acrylaldehyde (**3b**; m = 1): General Wittig homologation procedure. The product was prepared from **3a** and isolated as a pale yellow solid in 94.0% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.68 (d, J = 8.0 Hz, 1H), 7.44 (d, *J* = 15.8 Hz, 1H), 7.32 (dd, *J* = 1.4 Hz, 8.0 Hz, 1H), 7.22 (m, 2H), 6.68 (dd, *J* = 7.8 Hz, 15.8 Hz, 1H), 3.21 (s, 2H), 1.39 (s, 6H); ^{13}C NMR (300 MHz, $CDC1_3$): δ 193.6, 152.8, 149.1, 145.9, 130.7, 128.3, 127.0, 122.8, 122.4, 47.5, 47.1, 27.5.

(2E,4E)-5-(3,3-dimethyl-2,3-dihydrobenzo[b]thiophen-5-yl)penta-2,4-dienal (**3c**; m = 2): General Wittig homologation procedure. The product was prepared from **3b** and isolated as a yellow solid in 92.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.61 (d, *J* = 8.0 Hz, 1H), 7.26-7.16 (m, 2H), 6.96 (m, 2H), 6.26 (dd, *J* = 8.0 Hz, 15.2 Hz, 1H), 3.22 (s, 2H), 1.40 (s, 6H); ^{13}C NMR (400 MHz, $CDC1_3$): δ 193.81, 152.80, 149.30, 143.94, 142.88, 132.73, 131.23, 127.77, 125.10, 123.07, 121.80, 47.82, 47.46, 27.80.

(2E,4E,6E)-7-(3,3-dimethyl-2,3-dihydrobenzo[b]thiophen-5-yl)hepta-2,4,6-trienal (**3d**; m = 3): General Wittig homologation procedure. The product was prepared from **3c** and isolated as an orange solid in 90.0% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.87 (d, *J* = 7.8 Hz, 1H), 7.16 (m, 4H), 6.80 (m, 3H), 6.50 (dt, *J* = 2.7 Hz, 11.1 Hz, 1H), 6.12 (dd, *J* = 8.1 Hz, 15.0 Hz, 1H), 3.16 (s, 2H), 1.35 (s, 6H); ^{13}C NMR (300 MHz, $CDC1_3$): δ 193.78, 152.27, 149.17, 143.44, 142.71, 138.77, 133.49, 131.21, 129.86, 127.10, 126.72, 123.04, 121.37, 47.84, 47.48, 27.81.

(2E,4E,6E,8E)-9-(3,3-dimethyl-2,3-dihydrobenzo[b]thiophen-5-yl)nona-2,4,6,8-tetraenal (**3e**; m = 4): General Wittig homologation procedure. The product was prepared from **3d** and isolated as a red-orange solid in 63.0% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.55 (d, *J* = 8.1 Hz, 1H), 7.18-7.07 (m, 4H), 6.85-6.56 (m, 4H), 6.48 (d, *J* = 11.1 Hz, 1H), 6.41 (dd, *J* = 8.1 Hz, 11.7 Hz, 1H), 6.14 (dd, *J* = 8.1 Hz, 15.3 Hz, 1H), 3.16 (s, 2H), 1.36 (s, 6H); ^{13}C NMR (300 MHz, $CDC1_3$): δ 193.9, 152.4, 149.1, 143.3, 142.0, 139.7, 136.5, 133.9, 131.6, 131.2, 130.0, 127.4, 126.9, 123.0, 121.1, 47.8, 47.5, 27.8.



DPDCn-SC$_4$H$_8$; m = 0, 1, 2, 3, 4

(1Z,3E,5Z)-2,5-dicyano-1,6-di-(3,3-dimethyl-2,3-dihydrobenzo[b]thiophene)-hexa-1,3,5-triene (**DPDC3-SC$_4$H$_8$**; m = 0): General double Knoevenagel condensation procedure. This molecule was prepared from **3a** and isolated as a lemon yellow solid in 41.9% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61 (d, *J* = 1.7 Hz, 2H), 7.57 (dd, *J* = 1.7 Hz, 8.2 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 7.12 (s, 2H), 6.79 (s, 2H), 3.24 (s, 4H), 1.42 (s, 12H); ^{13}C NMR (300 MHz, $CDC1_3$): δ 149.13, 145.70, 144.91, 130.13, 129.79, 129.39, 123.18, 122.75, 116.58, 107.63, 47.52, 47.22, 27.46.

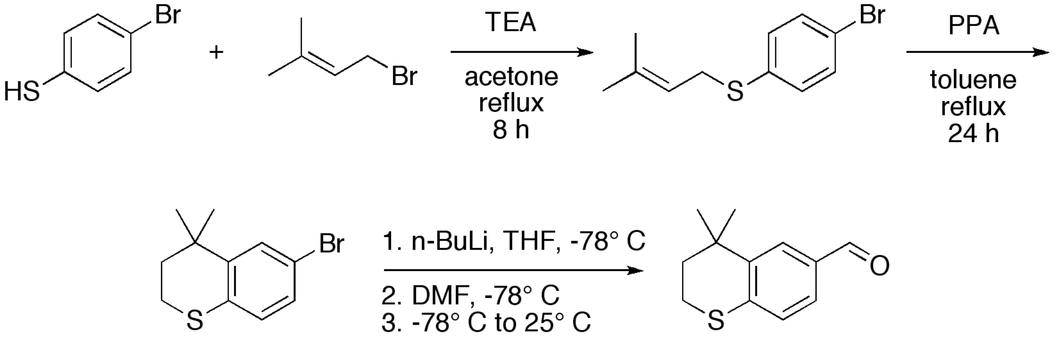
(1E,3Z,5E,7Z,9E)-4,7-dicyano-1,10-di-(3,3-dimethyl-2,3-dihydrobenzo[b]thiophene)-deca-1,3,5,7,9-pentaene (**DPDC5-SC$_4$H$_8$**; m = 1): General double Knoevenagel condensation procedure. The product was prepared from **3b** and isolated as a red solid in 30.0% yield. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.33 (dd, *J* = 1.5 Hz, 8.1 Hz, 2H), 7.28-7.19 (m, 6H), 7.05 (d, *J* = 11.4 Hz, 2H), 6.98 (d, *J* = 15.3 Hz, 2H), 6.70 (s, 2H), 3.24 (s, 4H), 1.41 (s, 12H); ^{13}C NMR (300 MHz, $CDC1_3$): δ 149.7, 146.0, 144.2, 142.2, 132.9, 129.3, 127.9, 123.8, 123.1, 122.0, 115.8, 111.3, 47.5, 47.0, 26.6.

(1E,3E,5Z,7E,9Z,11E,13E)-6,9-dicyano-1,14-di-(3,3-dimethyl-2,3-dihydrobenzo[b]thiophene)-tetradeca-1,3,5,7,9,11,13-heptaene (**DPDC7-SC$_4$H$_8$**; m = 2): General double Knoevenagel condensation procedure. The product was prepared from **3c** and isolated as a purple solid in 17.0% yield. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.12 (m, 6H), 7.05-6.77 (m, 10H), 6.67 (s, 2H), 3.23 (s, 4H), 1.41 (s, 12H); ^{13}C NMR (300 MHz, $CDC1_3$): δ 149.22, 145.17, 142.88, 142.87, 138.94, 133.57, 129.34, 128.73, 127.37, 127.14, 123.09, 121.29, 115.80, 111.35, 47.87, 47.50, 27.81.

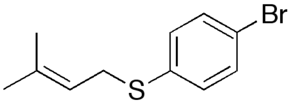
(1E,3E,5E,7Z,9E,11Z,13E,15E,17E)-8,11-dicyano-1,18-di-(3,3-dimethyl-2,3-dihydrobenzo[b]thiophene)-octadeca-1,3,5,7,9,11,13,15,17-nonaene (**DPDC9-SC$_4$H$_8$**; m

= 3): General double Knoevenagel condensation procedure. The product was prepared from **3d** and isolated as a dark purple solid in 10.5% yield. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.44 (d, *J* = 11.9 Hz, 2H), 7.35 (s, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 6.6 Hz, 2H), 7.09 (dd, *J* = 12.3 Hz, 17.2 Hz, 2H), 6.93 (dd, *J* = 13.5 Hz, 16.9 Hz, 2H), 6.85-6.62 (m, 12H), 3.22 (s, 4H), 2.08 (s, 12H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 149.10, 145.00, 142.62, 142.07, 139.94, 136.72, 133.96, 132.09, 129.42, 128.86, 127.59, 126.95, 123.01, 121.14, 115.79, 111.33, 47.85, 47.49, 27.80.

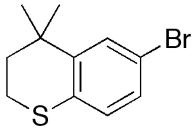
(1E,3E,5E,7E,9Z,11E,13Z,15E,17E,19E,21E)-10,13-dicyano-1,22-di-(3,3-dimethyl-2,3-dihydrobenzo[b]thiophene)-phenyl)-docosa-1,3,5,7,9,11,13,15,17,19,21-undecaene (**DPDC11-SC$_4$H$_8$**; m = 4): General double Knoevenagel condensation procedure. The product was prepared from **3e** and isolated as a dark purple-black solid in 8.0% yield. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.22-7.11 (m, 6H), 6.90-6.48 (m, 20H), 3.21 (s, 4H), 1.40 (s, 12H); ^{13}C NMR (500 MHz, CD_2Cl_2): δ 148.2, 144.0, 141.6, 140.7, 138.7, 136.7, 134.4, 133.4, 131.7, 128.6, 128.0, 127.1, 125.7, 122.0, 120.2, 114.8, 110.4, 47.0, 46.5, 26.9; one sp^2 carbon signal not observed.



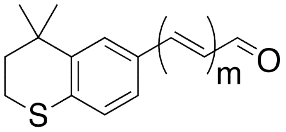
Scheme S2. Synthesis of 4,4-dimethylthiochroman-6-carbaldehyde.



1-bromo-4-[(3-methyl-2-buten-1-yl)thio]benzene: This compound is known [8] in the literature and has been prepared in poor yields by Fe-catalyzed sulfenylation of 4-bromothiophenol with isobutyl 1,1-dimethylprop-2-enyl hydrogen carbonate. We chose a different method for our preparation. 4-bromothiophenol (5.00 g, 26.4 mmol) and 3,3-dimethylallyl bromide (7.88 g, 52.9 mmol) was added to a 250-mL round-bottom flask with magnetic stir bar. The reaction flask was then charged with 200 mL of acetone and nitrogen was bubbled through for 25 min. 5 mL of triethylamine was added to reaction via syringe and the a white precipitate crashed out immediately. The reaction was stirred overnight at room temperature before filtering off the white solid and washing with acetone. Solvent was removed from the organic layer by rotary evaporation and then loaded onto a silica gel loading column. Column chromatography (100% hexanes) was used to isolate the product in quantitative yields. ^{1}H NMR (300 MHz, CD_2Cl_2): 7.39 (d, *J* = 8.7, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 5.27 (m, 1H), 3.50 (d, *J* = 7.7 Hz, 2H), 1.71 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (300 MHz, $CDC1_3$): 150.7, 140.1, 130.6, 126.4, 124.1, 118.1, 53.8, 47.9, 47.8, 27.6.



6-bromo-4,4-dimethylthiochroman: This compound is known, however NMR characterization was provided.[9] (4-bromophenyl)(3-methylbut-2-enyl)sulfane (2.72 g, 10.58 mmol) was in a 100-mL round-bottom flask and dissolved in a minimal amount of toluene (not dry). Polyphosphonic acid (5-10 mL) was added and the mixture was refluxed for 24 hours. The reaction was cooled to room temperature and toluene was decanted off. The remaining mixture was dissolved in water and extracted with toluene. Organics were combined, washed with sat. aqueous sodium chloride solution and dried over $MgSO_4$. After column chromatography in 100% hexanes the product was isolated in 2.37 g (87%) as a white powder. ^1H NMR (300 MHz, $CDCl_3$): 7.45 (d, *J* = 1.5 Hz, 1H), 7.14 (dd, *J* = 1.5 Hz, 6.3 Hz, 1H), 6.95 (d, *J* = 6.3 Hz, 1H), 3.01 (m, 2H), 1.92 (m, 2H), 1.31 (s, 6H); ^{13}C NMR (300 MHz, $CDC1_3$): 144.5, 131.5, 129.8, 129.4, 128.4, 117.7, 37.5, 33.6, 30.4, 23.4.



4a; m = 0
4b; m = 1
4c; m = 2
4d; m = 3
4e; m = 4
4f; m = 5

4,4-dimethylthiochroman-6-carbaldehyde (**4a**; m = 0): This compound is known, however NMR characterization was provided.[9] A 100-mL round-bottom flask was flame dried and charged with 6-bromo-4,4-dimethylthiochroman (1.00 g, 3.89 mmol) and anhydrous THF (50 mL). The reaction flask was cooled to -78° C in an acetone/dry ice bath for 40 min. 2.67 mL of n-BuLi (1.6 M in hexanes) solution was dripped into the reaction very slowly over 10 minutes. The reaction was allowed to stir at -78° C for 30 min before dry DMF (1 mL) was added dropwise. This reaction was allowed to warm to room temperature overnight. Reaction was quenched with water, allowed to stir for 10 min and extracted with ether. The organic layers were combined and washed with sat. sodium chloride solution and then dried over $MgSO_4$. Product was isolated by column chromatography to yield 0.686 g (86 %) of a colorless oil. ^1H NMR (300 MHz, $CDCl_3$):

9.87 (s, 1H), 7.85 (d, *J* = 1.8 Hz, 1H), 7.52 (dd, *J* = 1.8 Hz, 8.1 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 1H), 3.08 (m, 2H), 1.97 (m, 2H), 1.37 (s, 6H); ^{13}C NMR (500 MHz, CDC1$_3$): 191.5, 142.4, 141.7, 132.7, 127.6, 127.0, 126.9, 36.7, 33.1, 29.8, 23.3.

(E)-3-(4,4-dimethylthiochroman-6-carbaldehyde)acrylaldehyde (**4b**; m = 1): General Wittig homologation procedure. The product was prepared from **4a** and isolated as a pale yellow solid in 92.0% yield. ^{1}H NMR (300 MHz, CDCl$_3$): δ 9.64 (d, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 1.8 Hz, 1H), 7.42 (d, *J* = 15.6 Hz, 1H), 7.24 (dd, *J* = 1.8 Hz, 8.1 Hz, 1H), 7.12 (d, *J* = 8.1 Hz, 1H), 6.63 (dd, *J* = 7.5 Hz, 15.9 Hz, 1H), 3.05 (m, 2H), 1.94 (m, 2H), 1.33 (s, 6H); ^{13}C NMR (300 MHz, CDC1$_3$): δ 193.34, 153.81, 144.14, 138.88, 131.80, 128.94, 128.88, 128.85, 127.36, 41.45, 37.51, 34.28, 28.13.

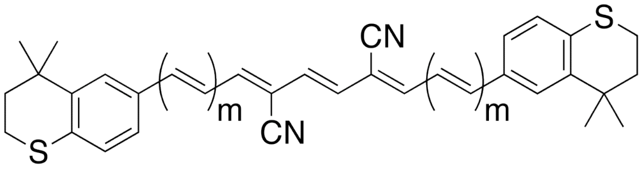
(2E,4E)-5-(4,4-dimethylthiochroman-6-carbaldehyde)penta-2,4-dienal (**4c**; m = 2): General Wittig homologation procedure. The product was prepared from **4b** and isolated as a yellow solid in 92.7% yield. ^{1}H NMR (300 MHz, CDCl$_3$): δ 9.62 (d, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 1.8 Hz, 1H), 7.19-7.30 (m, 2H), 7.11 (d, *J* = 8.1 Hz, 1H), 6.97-6.99 (m, 2H), 6.29 (dd, *J* = 7.8 Hz, 15.0 Hz, 1H), 3.06 (m, 2H), 1.97 (m, 2H), 1.36 (s, 6H); ^{13}C NMR (300 MHz, CDCl$_3$): δ 193.9, 152.9, 143.1, 142.8, 135.4, 131.9, 131.2, 127.5, 126.5, 125.1, 125.0, 37.6, 33.4, 30.4, 23.6.

(2E,4E,6E)-7-(4,4-dimethylthiochroman-6-carbaldehyde)hepta-2,4,6-trienal (**4d**; m = 3): General Wittig homologation procedure. The product was prepared from **4c** and isolated as a golden solid in 71.0% yield. ^{1}H NMR (300 MHz, CDCl$_3$): δ 9.55 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 1.2 Hz, 1H), 7.17-7.01 (m, 3H), 6.82-6.67 (m, 3H), 6.52 (m, 1H), 6.16 (dd, *J* = 7.8 Hz, 15.0 Hz, 1H), 3.00 (m, 2H), 1.91 (m, 2H), 1.31 (s, 6H); ^{13}C NMR (300 MHz, CDC1$_3$): δ 193.6, 152.3, 143.5, 142.7, 138.9, 134.0, 132.7, 131.1, 129.8, 127.3, 126.6, 126.0, 124.5, 37.7, 33.3, 30.3, 23.6.

(2E,4E,6E,8E)-9-(4,4-dimethylthiochroman-6-carbaldehyde)nona-2,4,6,8-tetraenal (**4e**; m = 4): General Wittig homologation procedure. The product was prepared from **4d** and isolated as an orange solid in 59.4% yield. ^{1}H NMR (300 MHz, CDCl$_3$): δ 9.55 (d, *J* = 8.1

Hz, 1H), 7.34 (d, *J* = 1.8 Hz, 1H), 7.20-7.08 (m, 2H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.83-6.56 (m, 4H), 6.48-6.36 (m, 2H), 6.17 (dd, *J* = 8.1 Hz, 15.0 Hz, 1H), 3.01 (m, 2H), 1.93 (m, 2H), 1.31 (s, 6H); ^{13}C NMR (500 MHz, $CDC1_3$): δ 193.42, 151.86, 142.87, 142.23, 139.29, 136.25, 132.90, 132.75, 131.10, 130.75, 129.52, 126.95, 126.88, 125.30, 123.97, 37.43, 33.00, 30.06, 23.20.

(2E,4E,6E,8E,10E)-9-(4,4-dimethylthiochroman-6-carbaldehyde)undeca-2,4,6,8,10-pentaenal (**4f**; m = 5): General Wittig homologation procedure. The product was prepared from **4e** and isolated as an orange solid in 41.3% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.60 (d, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 1.8 Hz, 1H), 7.25-7.15 (m, 2H), 7.06 (d, *J* = 8.1 Hz, 1H), 6.92-6.77 (m, 2H), 6.69-6.40 (m, 6H), 6.20 (dd, *J* = 8.1 Hz, 15.3 Hz, 1H), 3.07 (m, 2H), 1.98 (m, 2H), 1.37 (s, 6H); ^{13}C NMR (300 MHz, $CDC1_3$): δ 193.7, 152.1, 143.0, 142.7, 139.3, 137.3, 135.1, 133.4, 132.9, 132.4, 131.9, 131.1, 130.1, 127.7, 127.1, 125.6, 124.1, 37.8, 33.3, 30.2, 23.6.



DPDCn-SC$_8$H$_{10}$; m = 0, 1, 2, 3, 4, 5

(1Z,3E,5Z)-2,5-dicyano-1,6-di-(4,4-dimethylthiochroman)-hexa-1,3,5-triene (**DPDC3-SC$_5$H$_{10}$**; m = 0): General double Knoevenagel condensation procedure. The product was prepared from **4a** and isolated as a lemon yellow solid in 43.0% yield. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.92 (d, *J* = 1.8 Hz, 2H), 7.50 (dd, *J* = 2.1 Hz, 8.4 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.09 (s, 2H), 6.79 (s, 2H), 3.07 (m, 4H), 1.98 (m, 4H), 1.38 (s, 12H); ^{13}C NMR (300 MHz, CD$_2$C1$_2$): δ 145.3, 143.0, 137.6, 130.0, 129.8, 127.9, 127.2, 127.1, 116.9, 108.0, 37.3, 33.5, 30.0, 23.7.

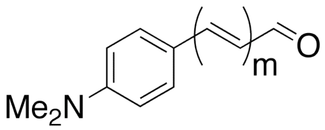
(1E,3Z,5E,7Z,9E)-4,7-dicyano-1,10-di-(4,4-dimethylthiochroman)-deca-1,3,5,7,9-pentaene (**DPDC5-SC$_5$H$_{10}$**; m = 1): General double Knoevenagel condensation procedure. The product was prepared from **4b** and isolated as a bright red solid in 34.8% yield. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 7.50 (d, *J* = 1.5 Hz, 2H), 7.32 (dd, *J* = 1.2 Hz, 8.4 Hz, 2H), 7.23 (dd, *J* = 11.4 Hz, 15.0 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 11.7 Hz, 2H), 6.97 (d, *J* = 15.3 Hz, 2H), 6.71 (s, 2H), 3.09 (m, 4H), 1.98 (m, 4H), 1.37 (s, 12H); ^{13}C NMR (300 MHz, CDC1$_3$): δ 145.7, 143.0, 142.4, 135.7, 132.1, 129.2, 127.3, 126.8, 124.8, 123.6, 115.5, 111.2, 37.6, 33.3, 30.0, 23.6.

(1E,3E,5Z,7E,9Z,11E,13E)-6,9-dicyano-1,14-di-(4,4-dimethylthiochroman)-tetradeca-1,3,5,7,9,11,13-heptaene (**DPDC7-SC$_5$H$_{10}$**; m = 2): General double Knoevenagel condensation procedure. The product was prepared from **4c** and isolated as a red-purple solid in 23.2%. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 7.43 (d, *J* = 1.8 Hz, 2H), 7.17 (dd, *J* = 1.8 Hz, 8.4 Hz, 2H), 7.04 (d, *J* = 8.1 Hz, 2H), 6.95-6.71 (m, 10H), 6.63 (s, 2H), 3.03 (m, 4H), 1.94 (m, 4H), 1.32 (s, 12H); ^{13}C NMR (300 MHz, CDC1$_3$): δ 146.7, 144.4, 144.2, 140.6, 135.5, 134.1, 130.5, 129.9, 128.8, 128.4, 127.4, 126.1, 117.4, 112.4, 38.9, 34.7, 31.8, 25.1.

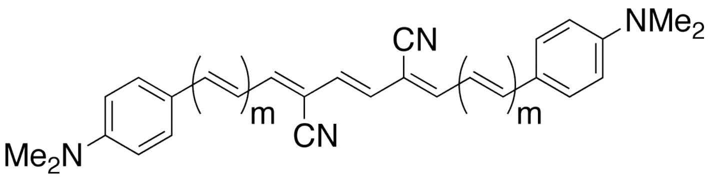
(1E,3E,5E,7Z,9E,11Z,13E,15E,17E)-8,11-dicyano-1,18-di-(4,4-dimethylthiochroman)-octadeca-1,3,5,7,9,11,13,15,17-nonaene (**DPDC9-SC$_5$H$_{10}$**; m = 3): General double Knoevenagel condensation procedure. The product was prepared from **4d** and isolated as a dark purple solid in 15.5% yield. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.39 (s, 2H), 7.19 (d, *J* = 9.0 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.91-6.62 (m, 14H), 6.55-6.47 (m, 2H), 3.07 (m, 4H), 1.97 (m, 4H), 1.34 (s, 12H); ^{13}C NMR (300 MHz, CDC1$_3$): δ 144.6, 142.3, 142.2, 139.5, 136.4, 132.8, 132.6, 131.5, 128.7, 128.2, 127.0, 126.8, 125.3, 123.9, 115.4, 110.5, 37.1, 32.8, 29.9, 23.1.

(1E,3E,5E,7E,9Z,11E,13Z,15E,17E,19E,21E)-10,13-dicyano-1,22-di-(4,4-dimethylthiochroman)-docosa-1,3,5,7,9,11,13,15,17,19,21-undecaene (**DPDC11-SC$_5$H$_{10}$**; m = 4): General double Knoevenagel condensation procedure. The product was prepared from **4e** and isolated as a lustrous blue-black solid in 6.0% yield. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 7.41 (d, *J* = 1.2 Hz, 2H), 7.18 (bd, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 2H), 6.92-6.45 (m, 20H), 3.08 (m, 4H), 2.01 (m, 4H), 1.40 (s, 12H); ^{13}C NMR (400 MHz, CDCl$_3$): δ 144.49, 142.19, 142.14, 139.32, 137.34, 135.09, 133.04, 133.02, 132.48, 132.21, 129.06, 128.61, 127.38, 126.93, 125.14, 123.92, 115.40, 110.93, 37.49, 33.00, 30.07, 23.20.

(1E,3E,5E,7E,9E,11Z,13E,15Z,17E,19E,21E,23E,25E)-12,15-dicyano-1,26-di-(4,4-dimethylthiochroman)-hexacosa-1,3,5,7,9,11,13,15,17,19,21,23,25-tridecaene (**DPDC13-SC$_5$H$_{10}$**; m = 5): General double Knoevenagel condensation procedure. The product was prepared from **4f** and isolated as a lustrous blue-black solid in 5.1% yield%. ^{1}H NMR (400 MHz, C$_2$D$_2$Cl$_4$): δ 7.38 (bs, 2H), 7.27-7.14 (m, 6H), 7.03 (d, *J* = 8.2 Hz, 2H), 6.88 (m, 2H), 6.82 (dd, *J* = 10.4 Hz, 15.3 Hz, 2H), 6.72-6.38 (m, 16H), 3.05 (m, 4H), 1.95 (m, 4H), 1.34 (s, 12H); ^{13}C NMR could not be obtained due to insolubility of product.



(2E,4E)-5-(4-(dimethylamino)phenyl)penta-2,4-dienal (**5a**; m = 2): Compound is known.[10] General Wittig homologation procedure. The product was prepared from *trans*-(4-dimethylamino)cinnamaldehyde and isolated as a golden-orange solid in 91.1% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.57 (d, *J* = 8.1 Hz, 1H), 7.41 (d, *J* = 8.9 Hz, 2H), 7.29 (dd, *J* = 7.5 Hz, 15.3 Hz, 1H), 6.97-6.73 (m, 2H), 6.71 (d, *J* = 8.9 Hz, 2H), 6.21 (dd, *J* = 8.1 Hz, 15.0 Hz, 1H), 3.02 (s, 6H); ^{13}C NMR (300 MHz, $CDC1_3$): δ 194.0, 154.1, 151.8, 143.9, 129.6, 129.5, 124.0, 122.0, 112.4, 40.6.



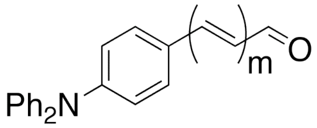
DPDCn-NMe$_2$; m = 0, 1, 2

(1Z,3E,5Z)-2,5-dicyano-1,6-di-(4-(dimethylamino)phenyl)-hexa-1,3,5-triene (**DPDC3-NMe$_2$**; m = 0): General double Knoevenagel condensation procedure. The product was prepared from (4-dimethylamino)benzaldehyde and isolated as an orange-red solid in 8.1% yield. ^{1}H NMR (300 MHz, $C_2D_2Cl_4$): δ 7.78 (d, *J* = 8.7 Hz, 4H), 7.02 (s, 2H), 6.72 (d, *J* = 8.7 Hz, 4H), 6.66 (s, 2H), 3.06 (s, 12H); ^{13}C NMR (500 MHz, $C_2D_2Cl_4$): δ 151.2, 143.7, 130.7, 127.7, 121.1, 117.1, 111.2, 102.9, 39.4.

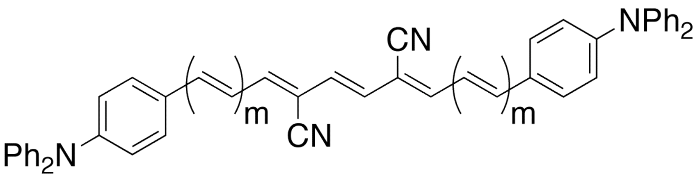
(1E,3Z,5E,7Z,9E)-4,7-dicyano-1,10-di-(4-(dimethylamino)phenyl)-deca-1,3,5,7,9-pentaene (**DPDC5-NMe$_2$**; m = 1): General double Knoevenagel condensation procedure. The product was prepared from *trans*-(4-dimethylamino)cinnamaldehyde and isolated as a lustrous blue-black solid in 30.1% yield. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$): δ 7.46 (d, *J* = 7.0 Hz, 4H), 7.17-6.83 (m, 6H), 6.73 (d, *J* = 7.0 Hz, 4H), 6.64 (s, 2H), 3.06 (s, 12H); ^{13}C NMR was not obtained due to insolubility.

(1E,3E,5Z,7E,9Z,11E,13E)-6,9-dicyano-1,14-di-(4-(dimethylamino)phenyl)-tetradeca-1,3,5,7,9,11,13-heptaene (**DPDC7-NMe$_2$**; m = 2): General double Knoevenagel

condensation procedure. The product was prepared from **5a** and isolated as a black lustrous solid in 23.3% yield. ^{1}H NMR (300 MHz, $C_2D_2Cl_4$): δ 7.40 (d, *J* = 8.7 Hz, 4H), 6.97-6.66 (m, 14H), 6.61 (s, 2H), 3.05 (s, 12H); ^{13}C NMR was not obtained due to limited solubility.



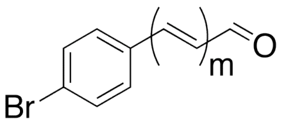
(E)-3-(4-(diphenylamino)phenyl)acrylaldehyde (**6a**; m = 1): Compound is known.[11] General Wittig homologation procedure. The product was prepared from 4-diphenylamino)benzaldehyde and isolated as a pale yellow solid in 55.3% yield. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 9.65 (d, *J* = 7.8 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.35-7.25 (m, 5H), 7.15-7.09 (m, 6H), 7.02 (d, *J* = 8.7 Hz, 2H), 6.62 (dd, *J* = 7.8 Hz, 15.6 Hz, 1H); ^{13}C NMR (300 MHz, $CDC1_3$): δ 194.0, 153.0, 151.2, 147.0, 130.2, 130.0, 127.1, 126.5, 126.1, 124.9, 121.4.



DPDCn-NPh$_2$; m = 0, 1

(1Z,3E,5Z)-2,5-dicyano-1,6-di-(4-(diphenylamino)phenyl)-hexa-1,3,5-triene (**DPDC3-NPh$_2$**; m = 0): General double Knoevenagel condensation procedure. The product was prepared from 4-diphenylamino)benzaldehyde and isolated as a orange-red solid in 16.3% yield. ^{1}H NMR (300 MHz, $C_2D_2Cl_4$): δ 7.76 (d, *J* = 8.8 Hz, 4H), 7.40-7.38 (m, 8H), 7.21-7.11 (m, 14H), 7.03 (d, *J* = 8.8 Hz, 4H), 6.79 (s, 2H); ^{13}C NMR (300 MHz, $CDC1_3$): δ 150.60, 146.87, 144.36, 131.06, 129.95, 129.61, 126.62, 126.27, 124.96, 120.84, 117.17, 106.53.

(1E,3Z,5E,7Z,9E)-4,7-dicyano-1,10-di-(4-(diphenylamino)phenyl)-deca-1,3,5,7,9-pentaene (**DPDC5-NPh$_2$**; m = 1): General double Knoevenagel condensation procedure. The product was prepared from **6a** and isolated as a dark purple solid in 51.6% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.3 Hz, 4H), 7.29 (t, *J* = 7.5 Hz, 8H), 7.14-7.08 (m, 14H), 7.00 (d, *J* = 8.3 Hz, 4H), 6.95 (d, *J* = 11.5 Hz, 2H), 6.89 (d, *J* = 15.2 Hz, 2H), 6.63 (s, 2H); ^{13}C NMR (500 MHz, $CDC1_3$): δ 149.44, 146.87, 145.38, 141.52, 129.50, 128.95, 128.83, 128.57, 125.37, 124.04, 122.69, 121.88, 115.64, 110.21.

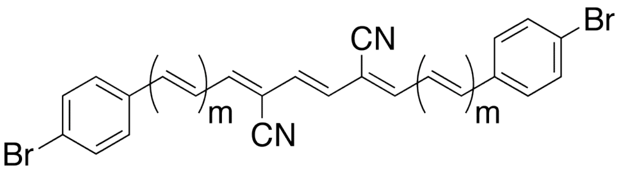


7a; m = 1
7b; m = 2
7c; m = 3

4-bromocinnamaldehyde (**7a**; m = 1): General Wittig homologation procedure. The product was prepared from 4-bromobenzaldehyde and isolated by column chromatograph (15% ethyl acetate in hexanes) as a white solid in 91.5% yield. This compound is known and matches the reported spectroscopic data.[12] ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.69 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.43-7.38 (m, 3H), 6.69 (dd, *J* = 7.6 Hz, 16.0 Hz, 1H); ^{13}C NMR (300 MHz, CDCl$_3$): δ 193.4, 151.2, 133.1, 132.5, 129.9, 129.2, 125.8.

(2E,4E)-5-(4-bromophenyl)penta-2,4-dienal (**7b**; m = 2): General Wittig homologation procedure. The product was prepared from **7a** and isolated by column chromatography (15% ethyl acetate in hexanes) as a yellow solid in 96.0% yield. This compound is known and matches the reported spectroscopic data.[13] ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.62 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.27-7.21 (dd, *J* = 9.6 Hz, 15 Hz, 1H), 7.02-6.91 (m, 2H), 6.31-6.25 (dd, *J* = 8.0 Hz, 15.0 Hz, 1H); ^{13}C NMR (400 MHz, CDCl$_3$): δ 193.5, 151.5, 140.9, 134.5, 132.1, 132.0, 128.9, 126.8, 123.8.

(2E,4E,6E)-7-(4-bromophenyl)hepta-2,4,6-trienal (**7c**; m = 3): General Wittig homologation procedure. The product prepared from **7b** and was isolated by column chromatograph (15% ethyl acetate in hexanes) as a orange-yellow solid in 73.7% yield. ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.60 (d, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.18 (dd, *J* = 11.0 Hz, 15.0 Hz, 1H), 6.92-6.72 (m, 3H), 6.58 (dd, *J* = 11.0 Hz, 14.0 Hz, 1H), 6.21, (dd, *J* = 7.6 Hz, 15.0 Hz, 1H); ^{13}C NMR (400 MHz, CDCl$_3$): δ 193.4, 151.3, 142.1, 136.8 135.3, 132.0, 131.4, 130.6, 128.3(4), 128.3(2), 122.7.



DPDCn-Br; m = 0, 1, 2, 3

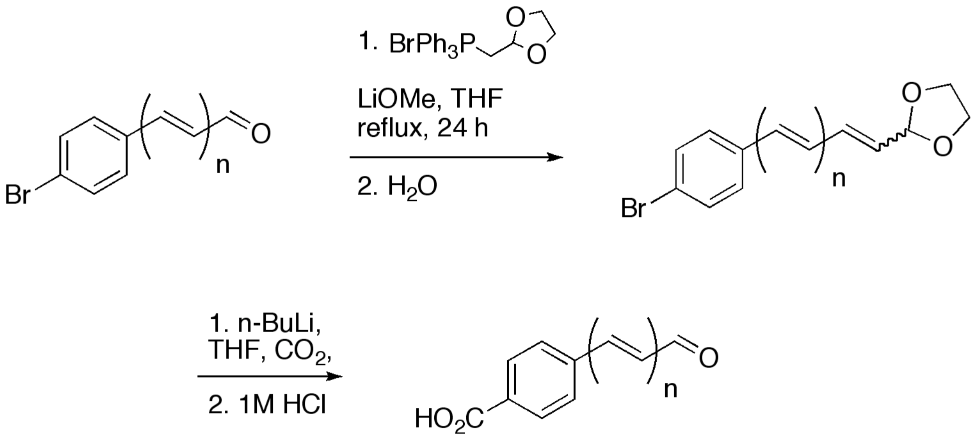
(1Z,3E,5Z)-2,5-dicyano-1,6-di-(4-bromophenyl)-hexa-1,3,5-triene (**DPDC3-Br**): General double Knoevenagel condensation procedure. The product was prepared from 4-bromobenzaldehyde and isolated as a yellow solid in 35.6% yield. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$): δ 7.72 (d, J = 8.4 Hz, 4H), 7.62 (d, J = 8.4 Hz, 4H), 7.19 (s, 2H), 6.86 (s, 2H); 13C NMR (400 MHz, DMSO-d_6): 7.81 (d, J = 8.4 Hz, 4H), 7.76 (s, 2H), 7.74 (d, J = 8.4 Hz, 4H), 6.97 (s, 2H); ^{13}C NMR (400 MHz, DMSO-d_6): δ 145.7, 133.2, 132.6, 131.4, 130.6, 124.8, 116.1, 110.2.

(1E,3Z,5E,7Z,9E)-4,7-dicyano-1,10-di-(4-bromophenyl)-deca-1,3,5,7,9-pentaene (**DPDC5-Br**): General double Knoevenagel condensation procedure. The product was prepared from **7a** and isolated as a peach-orange solid in 33.4% yield. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$): δ 7.58 (d, J = 8.4 Hz, 4H), 7.44 (d, J = 8.4 Hz, 4H), 7.28 (dd, J = 12.0 Hz, 15.0 Hz, 2H), 7.05 (d, J = 12.0 Hz, 2 H), 6.97 (d, J = 15.0 Hz, 2H), 6.75 (s, 2H); ^{13}C NMR (500 MHz, $C_2D_2Cl_4$): δ 146.2, 142.0, 136.2, 133.6, 130.8, 130.3, 126.8, 125.4, 116.2, 114.0

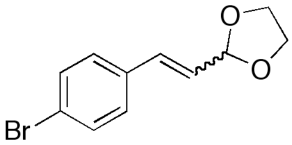
(1E,3E,5Z,7E,9Z,11E,13E)-6,9-dicyano-1,14-di-(4-bromophenyl)-tetradeca-1,3,5,7,9,11,13-heptaene (**DPDC7-Br**): General double Knoevenagel condensation procedure. The product was prepared from **7b** and isolated as a red solid in 15.5% yield. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$): δ 7.54 (d, J = 8.5 Hz, 4H), 7.36 (d, J = 8.5 Hz, 4H), 6.98-6.64 (m, 12H); ^{13}C NMR (500 MHz, $C_2D_2Cl_4$): δ 145.8, 143.5, 143.1, 138.6, 138.3, 133.5, 130.7, 130.2, 129.8, 124.2, 116.3, 113.4.

(1E,3E,5E,7Z,9E,11Z,13E,15E,17E)-8,11-dicyano-1,18-di-(4-bromophenyl)-octadeca-1,3,5,7,9,11,13,15,17-nonaene (**DPDC9-Br**): General double Knoevenagel condensation procedure. The product was prepared from **7c** and isolated as a red-purple solid in 7.6%

yield. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$): δ 7.52 (d, *J* = 8.4 Hz, 4H), 7.33 (d, *J* = 8.4 Hz, 4H), 6.99-6.55 (m, 16H); Limited solubility prevented acquisition of ^{13}C NMR.



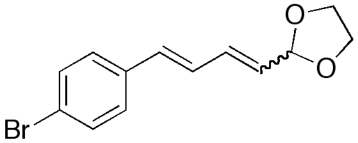
Scheme S3. General route to the synthesis of carboxylic acid aryl-enals through Wittig reaction and concomitant lithium-halogen exchange and carboxylation.



(E)-2-(4-bromostyryl)-1,3-dioxolane (***E*-7d**): Compound is known.[14] The product was synthesized from 4-bromobenzaldehyde using the general Wittig homologation procedure without acidic hydrolysis. Water was added to quench the reaction solution and the product was isolated by column chromatography (15% ethyl acetate in hexanes) as a white solid in 36.3% yield (both stereoisomers in overall 80.5% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.44 (d, J = 8.8 Hz, 2H), 7.27 (d, J = 8.8 Hz, 2H), 6.73 (d, J = 16.0 Hz, 1H), 6.15 (dd, J = 6.0 Hz, 16.0 Hz, 1H), 5.41 (d, J = 6.0 Hz, 1H), 4.09-3.19 (m, 4H); ^{13}C NMR (400 MHz, CDCl$_3$): δ 134.8, 133.5, 131.7, 128.4, 125.9, 122.3, 103.6, 65.1.

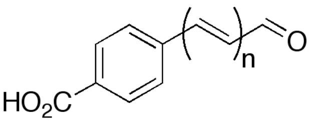
(Z)-2-(4-bromostyryl)-1,3-dioxolane (***Z*-7d**): Compound is known.[14] The product was synthesized from 4-bromobenzaldehyde using the general Wittig homologation procedure without acidic hydrolysis. The product was isolated by column chromatography (15% ethyl acetate in hexanes) as a colorless oil in 44.2% yield (both stereoisomers in overall 80.5% yield). ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.45 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 6.70 (d, J = 11.7 Hz, 1H), 5.73 (dd, J = 7.5 Hz, 11.7 Hz, 1H), 5.44 (d, J = 7.5

Hz, 1H), 4.09-3.84 (m, 4H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 135.0, 134.7, 131.8, 131.0, 129.0, 122.4, 99.9, 65.6.



2-((1E,3E)-4-(4-bromophenyl)buta-1,3-dienyl)-1,3-dioxolane (***E*-7e**): Acetals were synthesized from **7a** using the general Wittig homologation procedure without acidic hydrolysis. The product was isolated by column chromatography (15% ethyl acetate in hexanes) as a pale yellow solid in 36.4% yield (both stereoisomers in overall 93.5% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 6.77 (dd, *J* = 10.8 Hz, 15.6 Hz, 1H), 6.54 (m, 2H), 5.78 (dd, *J* = 6.0 Hz, 15.2 Hz, 1H), 5.35 (d, *J* = 6.0 Hz, 1H), 4.04-3.88 (m, 4H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 135.7, 135.5, 133.5, 131.8, 131.8, 129.4, 121.7, 103.4, 65.0; one sp^2-carbon signal not observed due to overlapping signals.

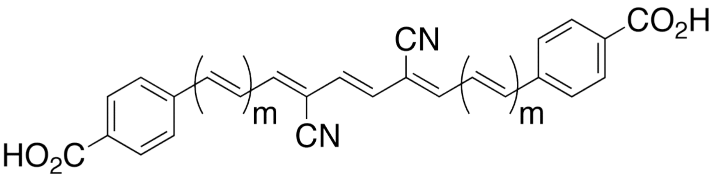
2-((1Z,3E)-4-(4-bromophenyl)buta-1,3-dienyl)-1,3-dioxolane (***Z*-7e**): Acetals were synthesized from **7a** using the general Wittig homologation procedure without acidic hydrolysis. The product was isolated by column chromatography (15% ethyl acetate in hexanes) as a pale yellow solid in 93.5% yield (both stereoisomers in overall 80.5% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.14 (dd, *J* = 11.2 Hz, 15.2 Hz, 1H), 6.55 (d, *J* = 15.0 Hz, 1H), 6.40 (t, *J* = 11.0 Hz, 1H), 5.78 (d, *J* = 6.4 Hz, 1H), 5.54 (dd, *J* = 4.4 Hz, 11.0 Hz, 1H), 4.10-3.91 (m, 4H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 135.8, 134.6, 134.1, 131.8, 128.2, 127.2, 124.0, 121.9, 99.5, 65.1.



(E)-4-(3-oxoprop-1-enyl)benzoic acid (**8a**; m = 1): This compound has been previously prepared by the soponification of methyl 4-(3-Oxo-1-propenyl)benzoate using sodium hydroxide.[15] In our method, a three-neck round-bottomed flask was charged with acetal

protected polyenal (either ***E*-7d** or ***Z*-7d**, 1.0 eq.) in dry THF and cooled to -78° C. n-butyl lithium (1.6 M in hexanes, 1.1 eq.) was added dropwise and the yellow solution was stirred for 15 minutes. Carbon dioxide gas (CO_2 tank, Matheson Tri-Gas; Product Grade) was bubbled into the solution until the yellow color disappeared, and then the reaction was left to warm to room temperature. The solution was diluted with diethyl ether, and then extracted (3x) with water. 1 M aq. hydrochloric acid was added to the aqueous layer and stirred for 1 h, during which time a precipitate formed. This was collected by vacuum filtration to yield pure product ($C_{10}O_2H_8$) as a white solid in 89.4% yield. [**Note**: When the Z-alkene is used, acetal hydrolysis may remain incomplete. In that event, the precipitate is dissolved in tetrahydrofuran before adding 1 M aq. hydrochloric acid. After stirring for 1 h, the solution was diluted with water and extracted (3x) with ethyl acetate. The organic layer was washed with brine, dried over magnesium sulfate, and concentrated to yield the all-*trans* product. It is important to note that both the (*E*)- and (*Z*)-acetals yield the same all-*trans*-product. Therefore, the *E*/*Z* mixture can be used as the starting material for **8a**.] ^{1}H NMR (300 MHz, Acetone-d_6): δ 11.39 (bs, 1H), 9.76 (d, *J* = 7.5 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 16.2 Hz, 1H), 6.88 (dd, *J* = 7.5 Hz, 16.2 Hz, 1H); ^{13}C NMR (300 MHz, Acetone-d_6): δ 193.5, 166.4, 151.1, 139.0, 132.8, 130.9, 130.6, 128.9.

4-((1E,3E)-5-oxopenta-1,3-dienyl)benzoic acid (**8b**; m = 2): A three-neck round-bottomed flask was charged with acetal protected polyenal (either ***E*-7e** or ***Z*-7e**, 1.0 eq.) in dry THF and cooled to -78° C. n-butyl lithium (1.6 M in hexanes, 1.1 eq.) was added dropwise and the yellow solution was stirred for 15 minutes. Carbon dioxide gas (CO_2 tank, Matheson Tri-Gas; Product Grade) was bubbled into the solution until the yellow color disappeared, and then the reaction was left to warm to room temperature. The solution was diluted with diethyl ether, and then extracted (3x) with water. To the water layer was added 1 M aq. hydrochloric acid and this was stirred for one hour during which time a precipitate formed. This was collected by vacuum filtration to yield pure product ($C_{12}O_2H_{10}$) as a yellow solid in 90.7% yield. [**Note**: When the Z-alkene is used, acetal hydrolysis may remain incomplete. In that event, the precipitate is dissolved in tetrahydrofuran before adding 1 M aq. hydrochloric acid. After stirring for 1 h, the solution was diluted with water and extracted (3x) with ethyl acetate. The organic layer was washed with brine, dried over magnesium sulfate, and concentrated to yield the all-*trans* product. It is important to note that both the (*E*)- and (*Z*)-acetals yield the same all-*trans*-product. Therefore, the *E*/*Z* mixture can be used as the starting material.] ^{1}H NMR (400 MHz, Acetone-d_6): δ 11.39 (bs, 1H), 9.68 (d, J = 8.0 Hz, 1H), 8.07 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.51 (dd, J = 10.8 Hz, 14.8 Hz, 1H), 7.43-7.36 (m, 1H), 7.26 (d, J = 15.6 Hz, 1H), 6.35 (dd, J = 8.0 Hz, 15.2 Hz, 1H); ^{13}C NMR (400 MHz, Acetone-d_6): δ 193.0, 166.3, 151.2, 137.3, 132.8, 130.8, 130.1, 129.0, 127.4, 125.2.

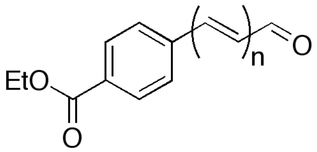


DPDCn-CO$_2$H; m = 0, 1, 2

(1Z,3E,5Z)-2,5-dicyano-1,6-di-(4-(carboxy)phenyl-hexa-1,3,5-triene (**DPDC3-CO$_2$H**; m = 0): A round-bottomed flask is charged with 4-formylbenzoic acid (1.0 eq.) and *trans*-1,4-dicyano-2-butene (1.0 eq.) in methanol under a nitrogen atmosphere. Sodium metal (>6.0 eq.) is dissolved in methanol and this is added directly to reaction solution. The reaction is stirred for 12 hours during which time a colored precipitate forms. The precipitate is collected by vacuum filtration, then suspended in methanol, and excess 1 M aq. hydrochloric acid is added. The reaction mixture is left to sit for one hour while the solid settles and is again collected by vacuum filtration. The yellow solid is pure product; 19.8% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.22 (bs, 2H), 8.05 (d, J = 8.4 Hz, 4H), 7.94 (m, 6H), 7.04 (s, 2H); ^{13}C NMR (400 MHz, DMSO-d_6): δ 167.0, 146.2, 137.8, 132.9, 131.1, 130.4, 129.7, 116.1, 111.2.

(1E,3Z,5E,7Z,9E)-4,7-dicyano-1,10-di-(4-(carboxy)phenyl)-deca-1,3,5,7,9-pentaene (**DPDC5-CO$_2$H**; m = 1): A round-bottomed flask is charged with **8a** acid (1.0 eq.) and *trans*-1,4-dicyano-2-butene (1.0 eq.) in methanol under a nitrogen atmosphere. Sodium metal (>6.0 eq.) is dissolved in methanol and this is added directly to reaction solution. The reaction is stirred for 12 hours during which time a colored precipitate forms. The precipitate is collected by vacuum filtration, then suspended in methanol, and excess 1 M aq. hydrochloric acid is added. The reaction mixture is left to sit for one hour while the solid settles and is again collected by vacuum filtration. The dark orange solid is pure product; 14.4% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.00 (bs, 2H) 7.95 (d, J = 8.0 Hz, 4H), 7.75 (d, J = 8.0 Hz, 4H), 7.61 (d, J = 10.4 Hz, 2H), 7.33-7.21 (m, 4H), 6.86 (s, 2H); ^{13}C NMR (400 MHz, DMSO-d_6): δ 167.3, 146.7, 141.5, 139.9, 131.8, 130.4, 129.8, 128.2, 127.0, 115.2, 112.7.

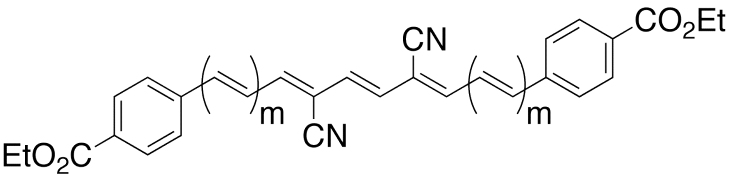
(1E,3E,5Z,7E,9Z,11E,13E)-6,9-dicyano-1,14-di-(4-(carboxy)phenyl)-tetradeca-1,3,5,7,9,11,13-heptaene (**DPDC7-CO_2H**; m = 2): A round-bottomed flask is charged with **8b** (1.0 eq.) and *trans*-1,4-dicyano-2-butene (1.0 eq.) in methanol under a nitrogen atmosphere. Sodium metal (>6.0 eq.) is dissolved in methanol and this is added directly to reaction solution. The reaction is stirred for 12 hours during which time a colored precipitate forms. The precipitate is collected by vacuum filtration, then suspended in methanol, and excess 1 M aq. hydrochloric acid is added. The reaction mixture is left to sit for one hour while the solid settles and is again collected by vacuum filtration. The dark red solid is pure product; 18.1% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.00 (bs, 2H), 7.91 (d, J = 8.4 Hz, 4H), 7.68 (d, J = 8.4 Hz, 4H), 7.51 (d, J = 11.6 Hz, 2H), 7.42 (dd, J = 11.0 Hz, 15.4 Hz, 2H), 7.04-7.00 (m, 4H), 6.87 (dd, J = 11.6 Hz, 14.8 Hz, 2H), 6.78 (s, 2H); Limited solubility prevented acquisition of ^{13}C NMR.



ethyl 4-formylbenzoate (**9a**; m = 0): Product prepared from reaction of 4-formylbenzoic acid with 1-bromoethane in the presence of base. Detailed preparation and characterization has been previously reported.[16]

(E)-ethyl 4-(3-oxoprop-1-enyl)benzoate (**9b**; m = 1): Product was prepared via Heck reaction involving ethyl 4-bromo-benzoate and acrolein diethyl acetal. Detailed preparation and characterization have been previously reported.[17] Yield: 85.1%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.73 (d, J = 7.6 Hz, 1H), 8.09 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4, 2H), 7.50 (d, J = 16.0 Hz, 1H), 6.77 (dd, J = 7.6 Hz, 16.0 Hz, 1H), 4.39 (q, J = 6.8 Hz, 2H), 1.38 (t, J = 6.8 Hz, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 193.3, 165.8, 150.9, 138.0, 132.6, 130.3, 130.2, 128.3, 61.3, 14.3.

ethyl 4-((1E,3E)-5-oxopenta-1,3-dienyl)benzoate (**9c**; m = 2): General Wittig homologation procedure was modified by using 3.0 eq. of (1,3-dioxolan-2-yl)methyl-triphenylphosphonium bromide and 3.3 eq. of LiOMe. The product was isolated by column chromatograph (15% ethyl acetate in hexanes) as a pale yellow solid in 64.6% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.64 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 8.0 Hz, 2H), 7.28 (dd, J = 9.5 Hz, 15.5 Hz, 1H), 7.07 (m, 2H), 6.32 (dd, J = 7.5 Hz, 15.5 Hz, 1H), 4.39 (q, J = 7.5 Hz, 2H), 1.41 (t, J = 7.5 Hz, 3H); ^{13}C NMR (500 MHz, $CDCl_3$): 193.4 166.0, 151.0, 140.8, 139.7, 132.7, 131.1, 130.1, 128.3, 127.3, 61.2, 14.3.

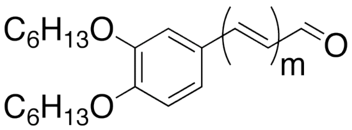


DPDCn-CO$_2$Et; m = 0, 1, 2

(1Z,3E,5Z)-2,5-dicyano-1,6-di-(4-(diethylbenzoate)-hexa-1,3,5-triene (**DPDC3-CO$_2$Et**; m = 0): General double Knoevenagel condensation procedure was modified by employing sodium methoxide as base; instead of DBU. The product was prepared from **9a** and was isolated as a bright yellow solid in 33.4% yield and was very insoluble. ^{1}H NMR (300 MHz, 355 K, $C_2D_2Cl_4$): δ 8.12 (bs, 4H), 7.92 (bs, 4H), 7.31 (bs, 2H), 6.94 (bs, 2H), 4.04 (bs, 4H), 1.42 (bs, 6H); ^{13}C NMR (400 MHz, $C_2D_2Cl_4$): δ 167.2, 145.9, 138.5, 134.0, 132.5, 131.5, 130.6, 116.7, 113.2, 62.7, 15.6.

(1E,3Z,5E,7Z,9E)-4,7-dicyano-1,10-di-(4-(diethylbenzoate)-deca-1,3,5,7,9-pentaene (**DPDC5-CO$_2$Et**; m = 1): General double Knoevenagel condensation procedure. The product was prepared from **9b** and isolated as an orange solid in 32.4% yield. ^{1}H NMR (300 MHz, $C_2D_2Cl_4$): δ 8.06 (d, J = 8.1 Hz, 4H), 7.62 (d, J = 8.1 Hz, 4H), 7.35 (dd, J = 11.5 Hz, 15.3 Hz, 2H), 7.08 (d, J = 11.5 Hz, 2H), 7.04 (d, J = 15.3 Hz, 2H), 6.75 (s, 2H), 4.39 (q, J = 7.2 Hz, 4H), 1.41 (t, J = 7.2 Hz, 6H); ^{13}C NMR (400 MHz, $C_2D_2Cl_4$): δ 165.49, 144.61, 140.36, 139.09, 130.58, 129.58, 129.08, 127.00, 126.15, 114.44, 112.45, 60.82, 13.86.

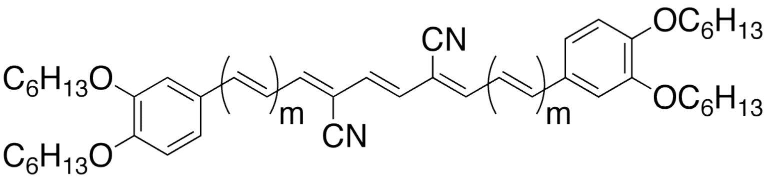
(1E,3E,5Z,7E,9Z,11E,13E)-6,9-dicyano-1,14-di-(4-(diethylbenzoate)-tetradeca-1,3,5,7,9,11,13-heptaene (**DPDC7-CO$_2$Et**; m = 2): General double Knoevenagel condensation procedure. The product was prepared from **9c** and isolated as a red solid in 14.6% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.04 (d, J = 8.0 Hz, 4H), 7.54 (d, J = 8.0 Hz, 4H), 7.11-6.72 (m, 12H), 4.41 (q, J = 7.0 Hz, 4H), 1.43 (t, J = 7.0 Hz, 6H); ^{1}H NMR (500 MHz, $C_2D_2Cl_4$): δ 8.03 (d, J = 8.2 Hz, 4H), 7.53 (d, J = 8.2 Hz, 4H), 7.08 (dd, J = 10.5 Hz, 15.3 Hz, 2H), 6.97-6.80 (m, 8H), 6.68 (s, 2H), 4.38 (q, J = 7.1 Hz, 4H), 1.40 (t, J = 7.1 Hz, 6H); ^{13}C NMR (500 MHz, $C_2D_2Cl_4$): δ 165.64, 144.26, 141.34, 140.05, 136.69, 129.76, 129.62, 129.59, 129.53, 128.84, 126.39, 114.65, 111.51, 60.71, 13.89.



3,4-bis(hexyloxy)benzaldehyde (**10a**; m = 0): This product was prepared by reaction of 3,4-dihydroxybenzaldehyde with 1-bromodecane under basic conditions. Detailed preparation and characterization has been reported by Binnemanns and coworkers.[1]

(E)-3-(3,4-bis(hexyloxy)phenyl)acrylaldehyde (**10b**; m = 1): General Wittig Homologation procedure. The product was prepared from **10a** and isolated as a pale yellow solid in 91.1% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.68 (d, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 15.9 Hz, 1H), 7.16 (dd, *J* = 1.8 Hz, 8.4 Hz, 1H), 7.11 (d, *J* = 1.8 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 6.62 (dd, *J* = 7.8 Hz, 15.9 Hz, 1H), 4.04 (m, 4H), 1.84 (m, 4H), 1.51 (m, 4H), 1.39 (m, 8H), 0.95 (m, 6H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 194.1, 153.6, 152.7, 149.6, 127.2, 126.8, 123.9, 113.1, 112.7, 69.7, 69.4, 32.0, 31.9, 29.5, 29.4, 26.1, 26.0, 23.0, 22.9, 14.4 (2 -CH_3 carbon signals).

(2E,4E)-5-(3,4-bis(hexyloxy)phenyl)penta-2,4-dienal (**10c**; m = 2): General Wittig procedure. The product was prepared from **10b** and isolated as a lemon yellow solid in 42.0% yield. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 9.62 (d, *J* = 8.1 Hz, 1H), 7.32 (dd, *J* = 10.2 Hz, 15.3 Hz, 1H), 7.10-6.88 (m, 5H), 6.25 (dd, *J* = 7.8 Hz, 15.0 Hz, 1H), 4.06 (m, 4H), 1.86 (m, 4H), 1.50 (m, 4H), 1.37 (m, 8H), 0.93 (m, 6H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 195.73, 154.96, 152.97, 151.07, 144.77, 132.05, 130.25, 125.79, 124.04, 115.28, 114.24, 71.36, 70.96, 33.36, 33.33, 31.07, 30.94, 27.49, 27.46, 24.45, 24.43, 15.9 (2 -CH_3 signals).



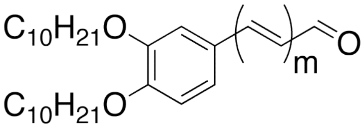
DPDCn-OC$_6$H$_{13}$; m = 0, 1, 2

(1Z,3E,5Z)-2,5-dicyano-1,6-di-(3,4-bis(hexyloxy)phenyl)-hexa-1,3,5-triene (**DPDC3-OC$_6$H$_{13}$**; m = 0): General double Knoevenagel condensation procedure. The product was prepared from **10a** and isolated as a lemon yellow solid in 7.8% yield. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.61 (d, J = 2.1 Hz, 2H), 7.32 (dd, J = 1.8 Hz, 8.4 Hz, 2H), 7.09 (s, 2H), 6.92 (d, J = 8.4 Hz, 2H), 6.77 (s, 2H), 4.06 (m, 8H), 1.86 (m, 8H), 1.52 (m, 8H), 1.37 (m, 16H), 0.94 (m, 12H); ^{13}C NMR (300 MHz, CDCl$_3$): δ 152.2, 149.4, 145.4, 139.3, 129.8, 126.8, 125.0, 113.1, 113.0, 107.0, 69.6, 69.4, 32.0, 31.9, 30.1, 29.6, 29.5, 26.1, 26.0, 23.0, 14.4 (2 -CH$_3$ carbon signals).

(1E,3Z,5E,7Z,9E)-4,7-dicyano-1,10-di-(3,4-bis(hexyloxy)phenyl)-deca-1,3,5,7,9-pentaene (**DPDC5-OC$_6$H$_{13}$**; m = 1): General double Knoevenagel condensation procedure. The product was prepared from **10b** and isolated as a dark red solid in 13.0% yield. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.28 (s, 2H), 7.17-7.07 (m, 6H), 7.00-6.86 (m, 6H), 6.67 (s, 2H), 4.09 (m, 8H), 1.87 (m, 8H), 1.52 (m, 8H), 1.38 (m, 16H), 0.93 (m, 12H); ^{13}C NMR (300 MHz, CDCl$_3$): δ 151.6, 149.7, 145.9, 142.6, 129.1, 129.0, 123.0, 122.7, 116.0, 113.4, 112.1, 110.7, 69.8, 69.5, 32.0, 31.9, 29.6, 29.5, 26.1, 26.0, 23.0 (2 -CH$_2$- signals), 14.4 (2 -CH$_3$ carbon signals).

(1E,3E,5Z,7E,9Z,11E,13E)-6,9-dicyano-1,14-di-(3,4-bis(hexyloxy)phenyl)-tetradeca-1,3,5,7,9,11,13-heptaene (**DPDC7-OC$_6$H$_{13}$**; m = 2): General double Knoevenagel condensation procedure. The product was prepared from **10c** and isolated as a dark purple solid in 20.1% yield. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.04 (d, J = 1.8 Hz, 2H), 7.01 (dd, J = 2.1 Hz, J = 8.7 Hz, 2H), 6.95-6.75 (m, 12H), 6.65 (s, 2H), 4.04 (m, 8H), 1.87 (m, 8H), 1.51 (m, 8H), 1.37 (m, 16H), 0.93 (m, 12H); ^{13}C NMR (CDCl$_3$); δ 300 MHz: 150.76, 149.67, 145.22, 142.99, 139.08, 129.21, 128.32, 126.53, 121.77, 115.88, 115.00, 113.65,

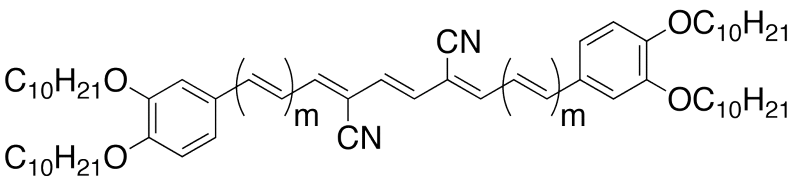
111.70, 111.06, 69.68, 69.54, 32.00, 31.98, 29.63, 29.54, 26.11, 26.08, 23.03, 23.02, 14.45, 14.43.



3,4-bis(decyloxy)benzaldehyde (**11a**; m = 0): This product was prepared by reaction of 3,4-dihydroxybenzaldehyde with 1-bromohexane under basic conditions. Detailed preparation and characterization has been reported by Binnemanns and coworkers.[1]

(E)-3,4-bis(decyloxy)cinnamaldehyde (**11b**; m = 1): General Wittig homologation procedure. The product was prepared from **11a** and isolated as a pale yellow solid in 98.8% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.68 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 15.6 Hz, 1H), 7.13 (dd, *J* = 2.0 Hz, 8.4 Hz, 1H), 7.09 (d, *J* = 1.6 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.60 (dd, *J* = 8.0 Hz, 16 Hz, 1H), 4.04 (m, 4H), 1.84 (m, 4H), 1.48 (m, 4H), 1.36-1.28 (m, 24H), 0.88 (t, *J* = 6.4 Hz, 6H); ^{13}C NMR (500 MHz, $CDC1_3$): δ 193.57, 153.06, 152.34, 149.34, 126.88, 126.52, 123.44, 112.93, 112.54, 69.43, 69.12, 31.91, 29.62, 29.60, 29.58, 29.40, 29.37, 29.35, 29.22, 29.20, 26.01, 25.98, 22.68 (2 -CH_2- carbon signals), 14.10 (2 -CH_3 carbon signals); three other aliphatic carbon signals not observed due to overlapping shifts.

(2E,4E)-5-(3,4-bis(decyloxy)phenyl)penta-2,4-dienal (**11c**; m = 2): General Wittig homologation procedure. The product was prepared from **11b** and isolated as a yellow solid in 96.4% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.58 (d, *J* = 8.1 Hz, 1H), 7.25 (dd, *J* = 10.4 Hz, 15.1 Hz, 1H), 7.05 (d, *J* = 1.9 Hz, 1H), 7.03 (dd, *J* = 1.9 Hz, 8.1 Hz, 1H), 6.97 (d, *J* = 15.4 Hz, 1H), 6.88-6.67 (m, 2H), 6.87-6.83 (m, 2H), 6.26 (d, *J* = 8.1 Hz, 15.3 Hz, 1H), 4.03 (m, 4H), 1.82 (m, 4H), 1.48 (m, 4H), 1.41-1.16 (m, 24H), 0.88 (t, *J* = 6.9 Hz, 6H); ^{13}C NMR (500 MHz, $CDC1_3$): δ 193.54, 152.62, 151.10, 149.35, 142.72, 130.53, 128.60, 124.06, 122.05, 113.23, 112.02, 69.46, 69.16, 31.92, 29.63, 29.62, 29.59, 29.57, 29.43, 29.35, 29.34, 29.30, 29.18, 26.05, 26.013, 22.69 (2 -CH_2- carbon signals), 14.10 (2 -CH_3 carbon signals); two other aliphatic carbon signals not observed due to overlapping shifts.

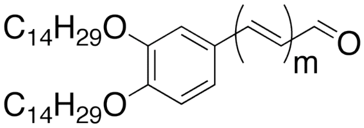


DPDCn-OC$_{10}$H$_{21}$; m = 0, 1, 2

(1Z,3E,5Z)-2,5-dicyano-1,6-di-(3,4-bis(decyloxy)phenyl)-hexa-1,3,5-triene (**DPDC3-OC$_{10}$H$_{21}$**; m = 0): General double Knoevenagel condensation procedure. The product was prepared from **11a**. Reaction took longer than other double Knoevenagel condensations and was stirred for 48 h at 50° C. The product was isolated as a lemon yellow solid in 18.7% yield. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.59 (d, *J* = 1.6 Hz, 2H), 7.30 (dd, J = 1.6 Hz, *J* = 8.4 Hz, 2H), 7.08 (s, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.76 (s, 2H), 4.07 (m, 8H), 1.85 (m, 8H), 1.49 (m, 8H), 1.40-1.20 (m, 48H), 0.88 (t, *J* = 6.4 Hz, 12H); ^{13}C NMR (300 MHz, CDCl$_3$): δ 152.17, 149.46, 145.32, 129.75, 126.77, 124.97, 117.24, 113.33, 113.11, 106.99, 69.64, 69.47, 32.32, 30.11, 30.03, 30.01, 29.99, 29.77, 29.54, 29.46, 28.77, 26.44, 26.37, 26.18, 23.10, 22.57, 14.52 (2 -CH$_3$ carbon signals); two aliphatic carbon signals were not observed due to overlapping chemical shifts.

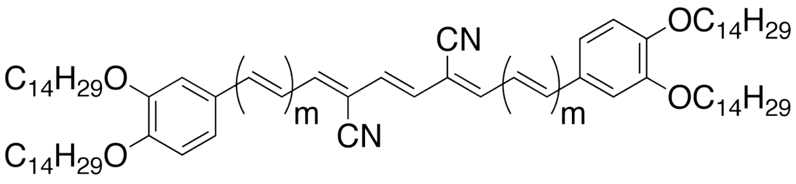
(1E,3Z,5E,7Z,9E)-4,7-dicyano-1,10-di-(3,4-bis(decyloxy)phenyl)-deca-1,3,5,7,9-pentaene (**DPDC5-OC$_{10}$H$_{21}$**; m = 1): General double Knoevenagel condensation procedure. The product was prepared from **11b**. Reaction took longer than other double Knoevenagel condensations and was run for 48 h at 50° C. The product was isolated as a purple solid in 9.6% yield. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.16-7.04 (m, 6H), 6.97-6.84 (m, 6H), 6.52 (s, 2H), 4.04 (m, 8H), 1.86 (m, 8H), 1.50 (m, 8H), 1.38 (m, 48H), 0.88 (m, 12H); ^{13}C NMR (400 MHz, CDCl$_3$): δ 151.27, 149.42, 145.49, 142.20, 128.71, 128.63, 122.68, 122.31, 115.59, 113.21, 111.99, 110.32, 69.48, 69.15, 31.92, 29.63, 29.61, 29.58, 29.44, 29.40, 29.36, 29.34, 29.32, 29.17, 26.05, 26.00, 22.69 (2 -CH$_2$- carbon signals), 14.10 (2 -CH$_3$ carbon signals); two aliphatic carbon signals were not observed due to overlapping chemical shifts.

(1E,3E,5Z,7E,9Z,11E,13E)-6,9-dicyano-1,14-di-(3,4-bis(decyloxy)phenyl)-tetradeca-1,3,5,7,9,11,13-heptaene (**DPDC7-OC$_{10}$H$_{21}$**; m = 2): General double Knoevenagel condensation procedure. The product was prepared from **11c**. Reaction took longer than other double Knoevenagel condensations and was run for 48 h at 50° C. The product was isolated as a purple solid in 25.6% yield. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.03-6.65 (m, 18H), 4.05 (m, 8H), 1.86 (m, 8H), 1.51 (m, 8H), 1.30 (m, 48H), 0.91 (t, *J* = 6.4 Hz, 12H); ^{13}C NMR (300 MHz, CDCl$_3$): δ 150.1, 149.7, 145.2, 143.0, 139.1, 129.9, 129.2, 128.3, 126.5, 121.8, 115.9, 113.7, 111.8, 111.1, 69.7, 69.6, 32.3, 30.0 2 -CH$_3$ carbon signals, 29.8 (2 -CH$_3$ carbon signals), 29.7, 29.6, 26.4 (2 -CH$_3$ carbon signals), 23.1, 14.5 (2 -CH$_3$ carbon signals); five aliphatic carbon signals were not observed due to overlapping chemical shifts.



3,4-bis(tetradecyloxy)benzaldehyde (**12a**; m = 0): This product was prepared by reaction of 3,4-dihydroxybenzaldehyde with 1-bromotetradecane under basic conditions. Detailed preparation and characterization has been reported by Binnemanns and coworkers.[1]

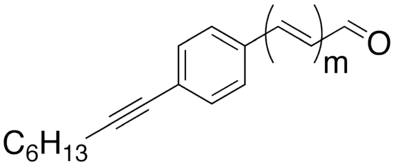
3,4-bis(tetradecyloxy)cinnamaldehyde (**12b**; m = 1): General Wittig homologation procedure. The product was prepared from **12a** and isolated by column chromatography (5% ethylacetate in hexnes) as a light yellow solid in 53.4% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.66 (d, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 15.9 Hz, 1H), 7.13 (dd, *J* = 2.1 Hz, 8.1 Hz, 1H), 7.08 (d, *J* = 1.8 Hz, 1H), 6.89 (d, *J* = 8.1 Hz, 1H), 6.63 (dd, *J* = 7.8 Hz, 15.9 Hz, 1H), 4.04 (m, 4H), 1.84 (m, 4H), 1.78-1.02 (m, 44H), 0.88 (t, *J* = 6.9 Hz, 6H); ^{13}C NMR (300 MHz, $CDC1_3$): δ 193.79, 153.31, 152.75, 149.78, 127.31, 126.93, 123.78, 113.32, 123.96, 69.81, 69.50, 35.06, 34.91, 32.33, 31.98, 30.11, 29.81, 29.77, 29.63, 29.51, 29.45, 26.42, 26.39, 25.66, 23.07, 23.03, 21.03 (2 -CH_2- carbon signals), 14.43 (2 -CH_3 carbon signals); seven aliphatic peaks not observed due to overlapping chemical shifts.



DPDCn-OC$_{14}$H$_{29}$; m = 0, 1

(1Z,3E,5Z)-2,5-dicyano-1,6-di-(3,4-bis(tetradecyloxy)phenyl)-hexa-1,3,5-triene (**DPDC3-OC$_{14}$H$_{29}$**; m = 0): General double Knoevenagel condensation procedure. The product was prepared from **12a**. Reaction took longer than other double Knoevenagel condensations and was run for 36 h at 60° C. The product was isolated as a lemon yellow solid in 15.9% yield with a small amount of starting material as impurity. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.60 (d, *J* = 1.8 Hz, 2H), 7.33 (dd, *J* = 1.8 Hz, 8.4 Hz, 2H), 7.09 (s, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.78 (s, 2H), 4.08 (m, 8H), 1.86 (m, 8H), 1.49 (m, 8H), 1.28 (m, 80H), 0.90 (t, *J* = 6.9 Hz, 12H); ^{13}C NMR (300 MHz, CDCl$_3$): δ 151.96, 149.26, 144.83, 129.40, 126.51, 124.52, 116.73, 113.43, 113.08, 106.73, 69.41, 69.20, 31.89, 29.67, 29.62, 29.59, 29.57, 29.38, 29.34, 29.31, 29.19, 29.12, 26.03, 25.96, 22.63 (2 -CH$_2$- signals), 14.01 (2 -CH$_3$ signals); ten carbon signals not observed due to overlapping chemical shifts.

(1E,3Z,5E,7Z,9E)-4,7-dicyano-1,10-di-(3,4-bis(tetradecyloxy)phenyl)-deca-1,3,5,7,9-pentaene (**DPDC5-OC$_{14}$H$_{29}$**; m = 1): General double Knoevenagel condensation procedure. The product was prepared from **12b**. Reaction took longer than other double Knoevenagel condensations and was run for 36 h at 60° C. The product was isolated as a purple solid in 24.5% yield. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.16 (dd, *J* = 11.4 Hz, 15.0 Hz, 2H), 7.07 (m, 4H), 6.98-6.84 (m, 6H), 6.65 (s, 2H), 4.04 (m, 8H), 1.84 (m, 8H), 1.50 (m, 8H), 1.42-1.18 (m, 80H), 0.88 (m, 12H); ^{13}C NMR (400 MHz, CDCl$_3$): δ 151.27, 149.42, 145.49, 142.19, 128.71, 128.63, 122.67, 122.31, 115.59, 113.21, 111.99, 110.33, 69.48, 69.15, 31.93, 29.72, 29.67, 29.64, 29.62, 29.45, 29.40, 29.37, 29.32, 29.18, 26.05, 26.01, 22.69 (2 -CH$_2$- signals), 14.11 (2 -CH$_3$ signals); ten carbon signals not observed due to overlapping chemical shifts.

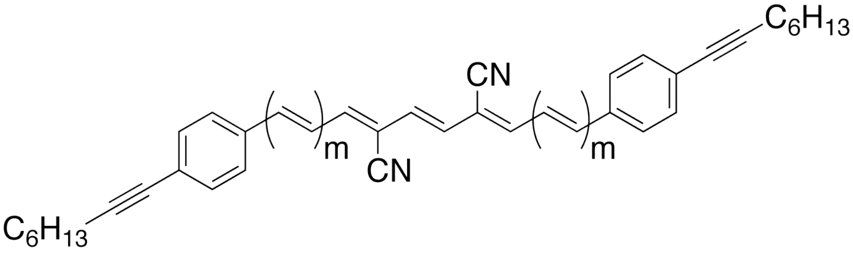


4-(oct-1-ynyl)benzaldehyde (**13a**; m = 0): This compound was prepared by modifying the reported procedure.[18] 4-bromobenzaldehyde (1.0 g, 5.4 mmol), PPh_3 (10 mol%), $PdCl_2(PPh_3)_2$ (5 mol%) and 25 mL of THF combined into a flame dried 100-mL round-bottomed flask to make a yellow suspension. The suspension was degassed with nitrogen gas for 10 min before copper(I) iodide (10 mol%) was added and the suspension was further degassed for another 10 min. During this time the suspended solid dissolved into an orange solution. 1-octyne was added via syringe and the reaction was heated at 40° C for 16 h. The resulting brown solution was cooled to room temperature and diluted with diethyl ether, washed with water and dried over $MgSO_4$. After removing the solvent under reduced pressure the product was isolated by flash column chromatography in hexanes/ethyl acetate (3:1), yielding a crude product as a light brown/yellow oil (99.0%). Spectroscopic data agrees with the literature. This product was not purified further but used in the next step as is. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.97 (s, 1H), 7.80 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 2.43 (t, J = 7.2 Hz, 2H), 1.60 (m, 2H), 1.45 (m, 2H), 1.30 (m, 4H), 0.91 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDC1_3$): δ 191.7, 135.4, 132.4, 131.0, 129.8, 95.7, 80.5, 31.7, 29.0, 28.9, 22.9, 19.9, 14.5.

(E)-(4-(oct-1-ynyl)phenyl)acrylaldehyde (**13b**; m = 1): General Wittig homologation procedure. The product was prepared from **13a** and isolated by column chromatography (10% ethyl acetate in hexanes) as an orange oil in 31.6% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.73 (d, J = 7.8 Hz, 1H), 7.52-7.43 (m, 5H), 6.72 (dd, J = 7.8 Hz, 15.9 Hz, 1H), 2.44 (t, J = 7.2 Hz, 2H), 1.63 (m, 2H), 1.46 (m, 2H), 1.34 (m, 4H), 0.92 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDC1_3$): δ 193.9, 152.3, 133.3, 132.5, 129.0, 128.7, 127.6, 94.3, 80.7, 31.7, 29.0, 28.9, 23.0, 19.9, 14.5.

(2E,4E)-5-(4-(oct-1-ynyl)phenyl)penta-2,4-dienal (**13c**; m = 2): General Wittig homologation procedure. The product was prepared from **13b** and isolated by column chromatography (10% ethyl actete in hexanes) as a dark orange oil in 74.1% yield. ^{1}H

NMR (300 MHz, $CDCl_3$): δ 9.65 (d, *J* = 8.1 Hz, 1H), 7.45-7.38 (m, 4H), 7.31-7.22 (ddd, *J* = 4.8 Hz, 6.7 Hz, 10.3 Hz, 1H), 6.99 (m, 2H), 6.31 (dd, *J* = 7.8 Hz, 15.3 Hz, 1H), 2.44 (t, *J* = 6.9 Hz, 2H), 1.63 (m, 2H), 1.47 (m, 2H), 1.33 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (300 MHz, $CDC1_3$): δ 193.8, 152.1, 142.0, 135.0, 132.4, 132.1, 127.7, 126.9, 125.9, 93.5, 80.8, 31.7, 29.1, 29.0, 22.9, 19.9, 14.4.



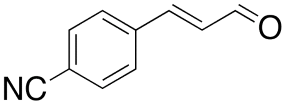
DPDCn-C$_8$H$_{13}$; m = 0, 1, 2

(1Z,3E,5Z)-2,5-dicyano-1,6-di-(4-(oct-1-ynyl)phenyl)-hexa-1,3,5-triene (**DPDC3-C$_8$H$_{13}$**; m = 0): General double Knoevenagel condensation procedure. The product was prepared from **13a** and isolated as a lemon yellow solid in 45.6% yield. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.79 (d, *J* = 8.4 Hz, 4H), 7.46 (d, *J* = 8.1 Hz, 4H), 7.15 (s, 2H), 6.84 (s, 2H), 2.44 (d, *J* = 6.6 Hz, 4H), 1.62 (m, 4H), 1.49 (m, 4H), 1.34 (m, 8H), 0.91 (t, *J* = 6.9 Hz, 6H); ^{13}C NMR (300 MHz, CDC1$_3$): δ 145.1, 132.6, 132.5, 130.9, 129.7, 127.5, 116.4, 109.9, 94.8, 80.8, 31.7, 29.0, 28.9, 22.9, 20.0, 14.4.

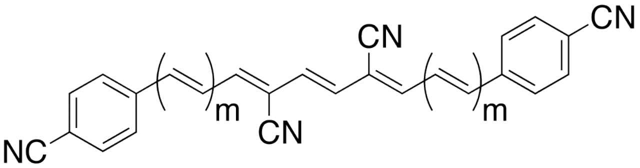
(1E,3Z,5E,7Z,9E)-4,7-dicyano-1,10-di-(4-(oct-1-ynyl)phenyl)-deca-1,3,5,7,9-pentaene (**DPDC5-C$_8$H$_{13}$**; m = 1): General double Knoevenagel condensation procedure. The product was prepared from **13b** and isolated as an orange-red solid in 7.6% yield. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.48 (d, *J* = 8.1 Hz, 4H), 7.42 (d, *J* = 8.4 Hz, 4H), 7.31 (dd, *J* = 11.7 Hz, 15.3 Hz, 2H), 7.02 (d, *J* = 15.6 Hz, 2H), 6.98 (d, *J* = 15.3 Hz, 2H), 6.71 (s, 2H), 2.45 (d, *J* = 6.9 Hz, 4H), 1.64 (m, 4H), 1.47 (m, 4H), 1.35 (m, 8H), 0.93 (t, *J* = 6.9 Hz, 6H); ^{13}C NMR (300 MHz, CDC1$_3$): δ 145.56, 141.77, 135.04, 132.48, 129.64, 127.90, 126.13, 125.39, 115.52, 112.41, 93.79, 80.92, 31.75, 29.03, 29.02, 22.94, 19.98, 14.44.

(1E,3E,5Z,7E,9Z,11E,13E)-6,9-dicyano-1,14-di-(4-(oct-1-ynyl)phenyl)-tetradeca-1,3,5,7,9,11,13-heptaene (**DPDC7-C$_8$H$_{13}$**; m = 2): General double Knoevenagel condensation procedure. The product was prepared from **13c** and isolated as a purple solid in 48.9% yield. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.37 (s, 8H), 6.98-6.75 (m, 10H), 6.65 (s, 2H), 2.42 (d, *J* = 6.6 Hz, 4H), 1.63 (m, 4H), 1.47 (m, 4H), 1.33 (m, 8H), 0.91 (t, *J*

= 6.6 Hz, 6H); ^{13}C NMR (300 MHz, $CDC1_3$): δ 145.1, 142.5, 138.3, 135.9, 132.4, 129.6, 129.5, 128.8, 127.3, 125.1, 115.6, 112.0, 93.1, 81.0, 31.7, 29.1, 29.0, 22.9, 20.0, 14.4.



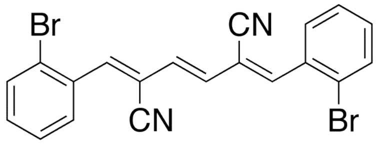
trans-4-cyanocinnamaldehyde (**14a**): General Wittig homologation procedure. The product was prepared from 4-cyanobenzadehyde and isolated by column chromatography (15% ethyl actete in hexanes) as a dark orange oil in 98.0% yield. ^{1}H NMR (300 MHz, CDCl$_3$): δ 9.78 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 16.2 Hz, 1H), 6.82 (dd, *J* = 7.8 Hz, 15.9 Hz, 1H); ^{13}C NMR (300 MHz, CDC1$_3$): δ 193.3, 149.8, 138.6, 133.2, 131.6, 129.1, 118.5, 114.7.



DPDCn-CN; m = 0, 1

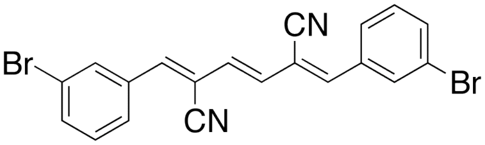
(1Z,3E,5Z)-2,5-dicyano-1,6-di-(4-cyanophenyl)-hexa-1,3,5-triene (**DPDC3-CN**; m = 0): General double Knoevenagel condensation procedure. The product was prepared from 4-cyanobenzaldehyde and isolated as a dull yellow solid in 21.8% yield. ^{1}H NMR (300 MHz, 355 K, DMSO-d_6): δ 8.01 (d, *J* = 7.8 Hz, 4H), 7.94 (d, *J* = 7.8 Hz, 4H), 7.85 (s, 2H), 7.06 (s, 2H); ^{13}C NMR (300 MHz, 355 K, DMSO-d$_6$): δ 145.7, 138.4, 133.5, 131.9, 130.6, 113.9, 113.1, 104.5, 106.0.

(1E,3Z,5E,7Z,9E)-4,7-dicyano-1,10-di-(4-cyanophenyl)-deca-1,3,5,7,9-pentaene
(**DPDC5-CN**; m = 1): General double Knoevenagel condensation procedure. The product was prepared from **14a** and isolated as an insoluble bright-orange solid in 25.8% yield. ^{1}H NMR (400 MHz, 355 K, DMF-d_7,): δ 8.05 (m, 8H), 7.81 (bd, 2H), 7.64 (bt, 2H), 7.53 (bd, 2H), 7.14 (bs, 2H); ^{13}C NMR was not obtained do to insolubility.



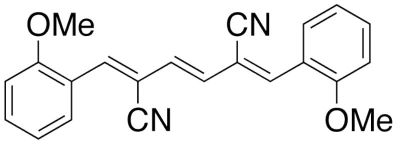
***ortho*-DPDC3-Br**

(1Z,3E,5Z)-2,5-dicyano-1,6-di-(2-bromophenyl)-hexa-1,3,5-triene (***ortho*-DPDC3-Br**): General double Knoevenagel condensation procedure. The product was prepared from 2-bromobenzaldehyde and isolated as a pale yellow solid in 33.9% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10 (dd, *J* = 1.5 Hz, 7.8 Hz, 2H), 7.70 (dd, *J* = 1.2 Hz, 8.1 Hz, 2H), 7.58 (s, 2H), 7.47 (td, *J* = 1.2 Hz, 7.8 Hz, 2H), 7.33 (td, *J* = 1.5 Hz, 7.8 Hz, 2H), 6.98 (s, 2H); ^{13}C NMR (300 MHz, 350 K, $C_2D_2C1_4$): δ 144.5, 133.3, 133.2, 131.7, 130.7, 129.3, 127.7, 125.2, 115.0, 112.6.



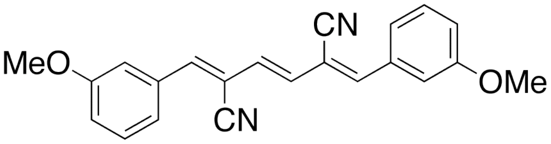
***meta*-DPDC3-Br**

(1Z,3E,5Z)-2,5-dicyano-1,6-di-(3-bromophenyl)-hexa-1,3,5-triene (***meta*-DPDC3-Br**): General double Knoevenagel condensation procedure. The product was prepared from 3-bromobenzaldehyde and isolated as a yellow solid in 24.9% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (dd, *J* = 1.7 Hz, 2H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.92 (t, *J* = 7.9 Hz, 2H), 7.15 (s, 2H), 6.88 (s, 2H); ^{13}C NMR (300 MHz, 350 K, $C_2D_2Cl_4$): d 143.3, 134.8, 133.3, 131.6, 130.2, 130.0, 127.1, 122.6, 114.7, 110.7.



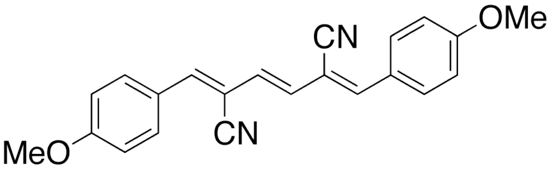
***ortho*-DPDC3-OMe**

(1Z,3E,5Z)-2,5-dicyano-1,6-di-(2-methoxyphenyl)-hexa-1,3,5-triene (***ortho*-DPDC3-OMe**): General double Knoevenagel condensation procedure. The product was prepared from 2-methoxybenzaldehyde and isolated as a yellow solid in 8.5% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (dd, *J* = 1.4 Hz, 7.8 Hz, 2H), 7.66 (s, 2H), 7.43-7.39 (m, 2H), 7.04 (t, *J* = 7.6 Hz, 2H), 6.94 (d, *J* = 8.3 Hz, 2H), 6.88 (s, 2H), 3.90 (s, 6H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 157.99, 140.11, 132.44, 130.28, 128.34, 122.69, 120.88, 116.47, 110.89, 109.46, 55.67.



***meta*-DPDC3-OMe**

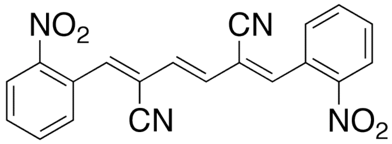
(1Z,3E,5Z)-2,5-dicyano-1,6-di-(3-methoxyphenyl)-hexa-1,3,5-triene (***meta*-DPDC3-OMe**): General double Knoevenagel condensation procedure. The product was prepared from 3-methoxybenzaldehyde and isolated as a neon yellow solid in 9.2% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (m, 2H), 7.40-7.33 (m, 4H), 7.19 (s, 2H), 7.00 (dt, *J* = 2.5 Hz, 6.6 Hz, 2H), 6.86 (s, 2H), 3.87 (s, 6H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 159.94, 145.60, 134.57, 130.42, 130.08, 122.52, 117.66, 116.06, 113.53, 109.76, 55.43.



***para*-DPDC3-OMe**

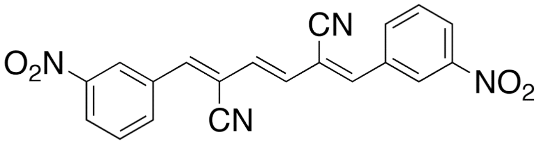
(1Z,3E,5Z)-2,5-dicyano-1,6-di-(4-methoxyphenyl)-hexa-1,3,5-triene (***para*-DPDC3-OMe**): General double Knoevenagel condensation procedure. The product was prepared from 4-methoxybenzaldehyde and isolated as a yellow solid in 11.4% yield. ^{1}H NMR

(400 MHz, DMSO-d_6): δ 7.83 (d, J = 8.4, 4H), 7.57 (s, 2H), 7.06 (d, J = 8.4, 4H), 6.82 (s, 2H), 3.85 (s, 6H); ^{13}C NMR (400 MHz, DMSO-d_6): δ 161.1, 144.7, 130.6, 128.5, 125.9, 115.8, 114.3, 105.8, 55.1.



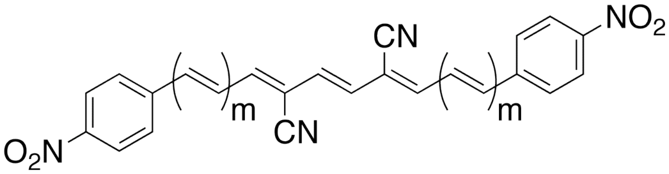
***ortho*-DPDC3-NO$_2$**

(1*Z*,3*E*,5*Z*)-2,5-dicyano-1,6-di-(2-nitrophenyl)-hexa-1,3,5-triene (***ortho*-DPDC3-NO$_2$**): This product could not be synthesized from 2-nitrobenzaldehyde using our method.



***meta*-DPDC3-NO$_2$**

(1Z,3E,5Z)-2,5-dicyano-1,6-di-(3-nitrophenyl)-hexa-1,3,5-triene (***meta*-DPDC3-NO$_2$**): General double Knoevenagel condensation procedure was modified. The base, DBU, was substituted with catalytic amounts sodium methoxide. The product was prepared from 3-nitrobenzaldehyde and isolated as a yellow solid in 10.9% yield. ^{1}H NMR (500 MHz, $C_2D_2C1_4$): δ 8.67 (s, 2H), 8.33 (d, *J* = 8.2 Hz, 2H), 8.22 (d, *J* = 7.8 Hz, 2H), 7.71 (t, *J* = 8.0 Hz, 2H), 7.37 (s, 2H), 6.99 (s, 2H); ^{13}C NMR (500 MHz, $C_2D_2C1_4$): δ 149.9, 144.7, 136.0, 135.9, 132.6, 131.8, 126.8, 125.4, 116.5, 113.8.

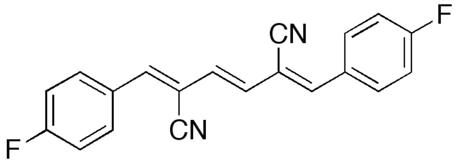


DPDCn-NO$_2$; m = 0, 1

(1Z,3E,5Z)-2,5-dicyano-1,6-di-(4-nitrophenyl)-hexa-1,3,5-triene (**DPDC3-NO$_2$**; m = 0): General double Knoevenagel condensation procedure was modified. The base, DBU, was substituted with catalytic amounts sodium methoxide. The product was prepared from 4-nitrobenzaldehyde and isolated as a yellow solid in 24.0% yield. ^{1}H NMR (500 MHz, $C_2D_2C1_4$): δ 8.33 (d, *J* = 8.5 Hz, 4H), 8.02 (d, *J* = 8.5 Hz, 4H), 7.36 (s, 2H), 7.00 (s, 2H);

^{13}C NMR (500 MHz, $C_2D_2C1_4$): δ 147.89, 142.98, 138.37, 131.22, 129.65, 123.78, 114.51, 112.67.

(1E,3Z,5E,7Z,9E)-4,7-dicyano-1,10-di-(4-nitrophenyl)-deca-1,3,5,7,9-pentaene (**DPDC5-NO_2**; m = 1): General double Knoevenagel condensation procedure was modified. The base, DBU, was substituted with catalytic amounts sodium methoxide. The product was prepared from *trans*-4-nitrocinnamaldehyde and isolated as a dark orange solid in 11.4% yield. ^{1}H NMR (400 MHz, 350 K, $C_2D_2C1_4$): δ 8.26 (d, J = 8.0 Hz, 4H), 7.71 (d, J = 8.0 Hz, 4H), 7.48-7.33 (m, 2H), 7.18-6.80 (m, 6H); ^{1}H NMR (400 MHz, 373 K, DMSO-d_6): δ 8.26 (d, J = 8.3 Hz, 4H), 7.93 (d, J = 8.3 Hz, 4H), 7.64 (d, J = 10.8 Hz, 2H), 7.44-7.32 (m, 4H), 6.94 (s, 2H); ^{13}C NMR could not be obtained due to limited solubility.



(1Z,3E,5Z)-2,5-dicyano-1,6-di-(4-fluorophenyl)-hexa-1,3,5-triene (**DPDC3-F**): General double Knoevenagel condensation procedure. The product was prepared from 4-fluorobenzaldehyde and isolated as a pale yellow solid in 33.4% yield. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.92 (bs, 4H), 7.75 (s, 2H), 7.35 (bs, 2H), 6.93 (s, 2H); ^{1}H NMR (500 MHz, $C_2D_2Cl_4$): δ 7.92 (m, 4H), 7.18 (m, 6H), 6.84 (s, 2H); ^{13}C NMR (400 MHz, $C_2D_2Cl_4$): δ 165.0, 143.4, 131.0, 130.9, 129.7, 115.8, 115.6 109.1; ^{19}F NMR (400 MHz, $C_2D_2Cl_4$): δ 106.2.

II. UV/Vis Absorption Spectrometry.

General Procedure and Instrumentation: Absorption spectra were taken on an Agilent Technologies 8453 UV-Vis spectrophotometer. Solutions of oligoenes were prepared in dichloromethane solution at a concentration between 10^{-5} and 10^{-6} M. A quartz quevette with path length equal to 1.0 cm was used in the collection of each spectrum.

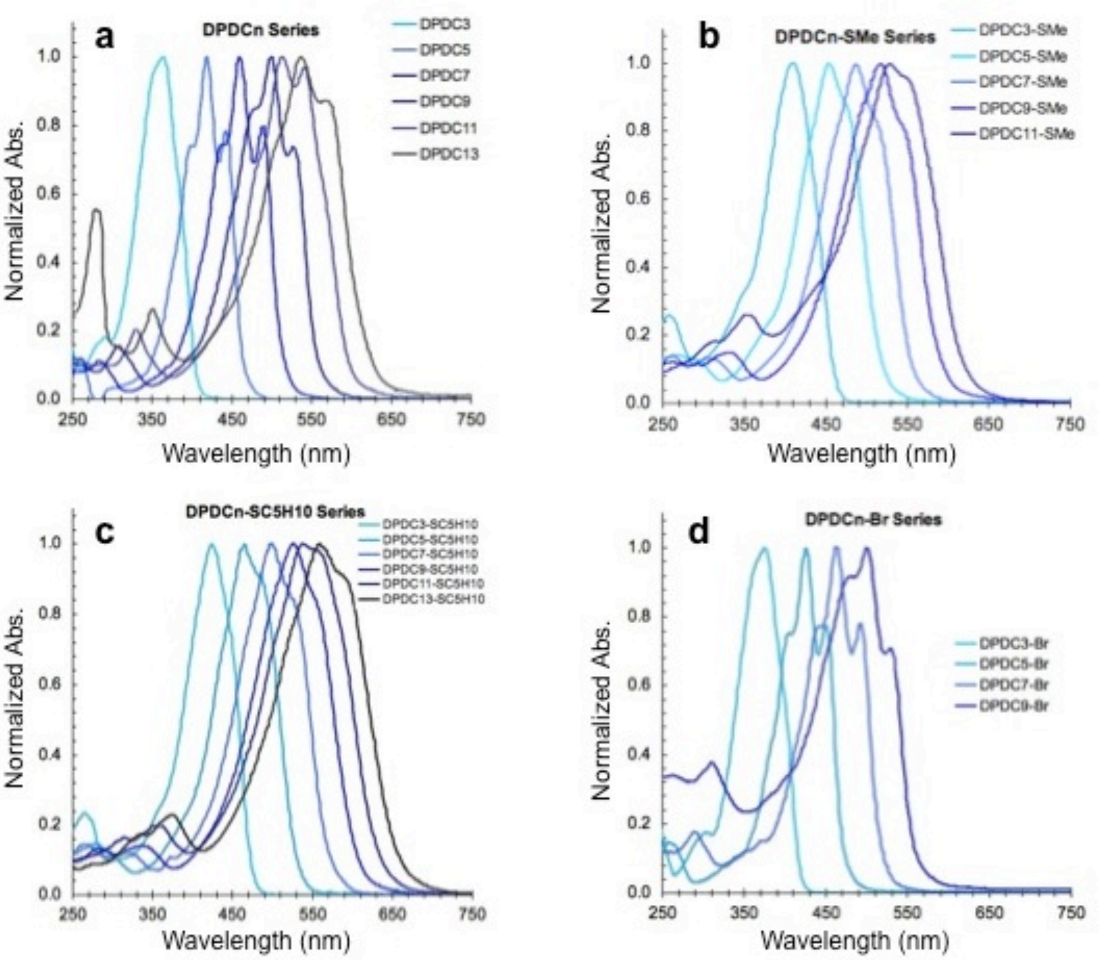


Figure S1. Optical abortion spectra of different families of α,ω-diphenyl-μ,ν-dicyano-oligoenes: (a) the unfunctionalized **DPDCn** series (n = 3 to 13), (b) **DPDCn-SMe** (n = 3 to 11), (c) **DPDCn-SC$_5$H$_{10}$** (n = 3 to 13) and (d) **DPDCn-Br** (n = 3 to 9). In all cases the spectra shift towards the red with increasing oligoene length (n). All spectra obtained in dichloromethane.

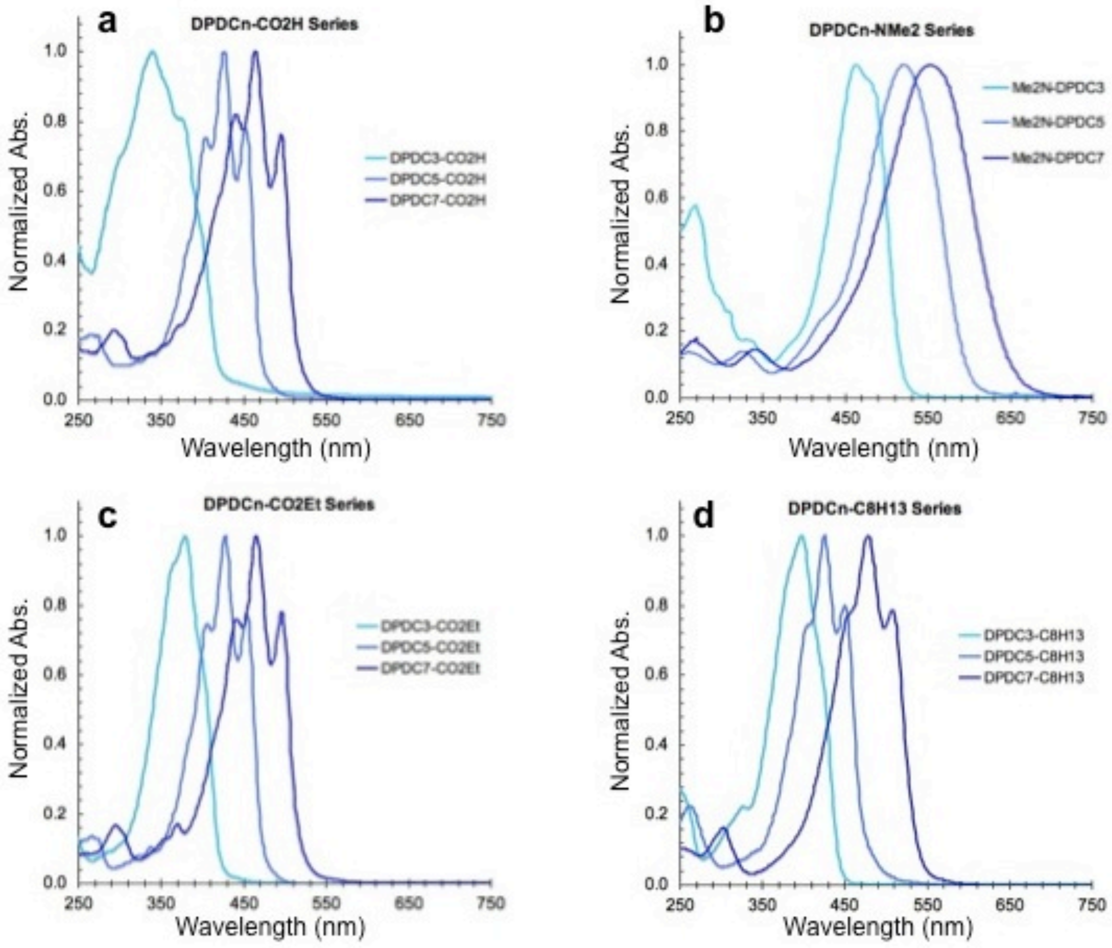


Figure S2. Optical abortion spectra of the (a) **DPDCn-CO$_2$H** series (n = 3, 5 and 7) in tetrahydrofuran solutions, as well as (b) **DPDCn-NMe$_2$** (n = 3, 5 and 7), (c) **DPDCn-CO$_2$Et** (n = 3, 5 and 7) and (d) **DPDCn-C$_8$H$_{13}$** (n = 3, 5 and 7) in dichloromethane solutions. In all cases the spectra shift towards the red with increasing oligoene length (n).

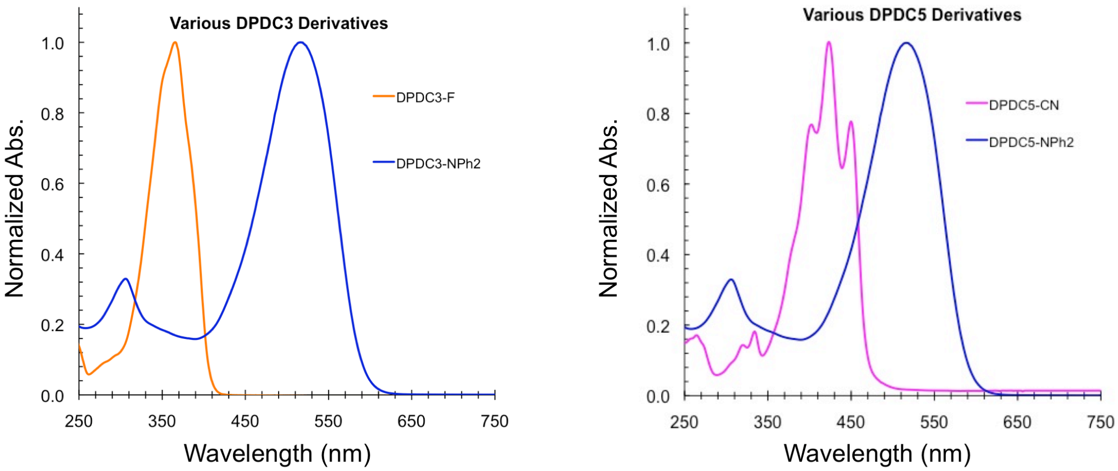


Figure S3. Optical abortion spectra of various (a) **DPDC3-X** derivatives, where X = **F** (orange line) and **NPh₂** (blue line); and (b) **DPDC5-X** derivatives, where X = **CN** (purple line) and **NPh₂** (dark blue line). All spectra obtained in dichloromethane solutions.

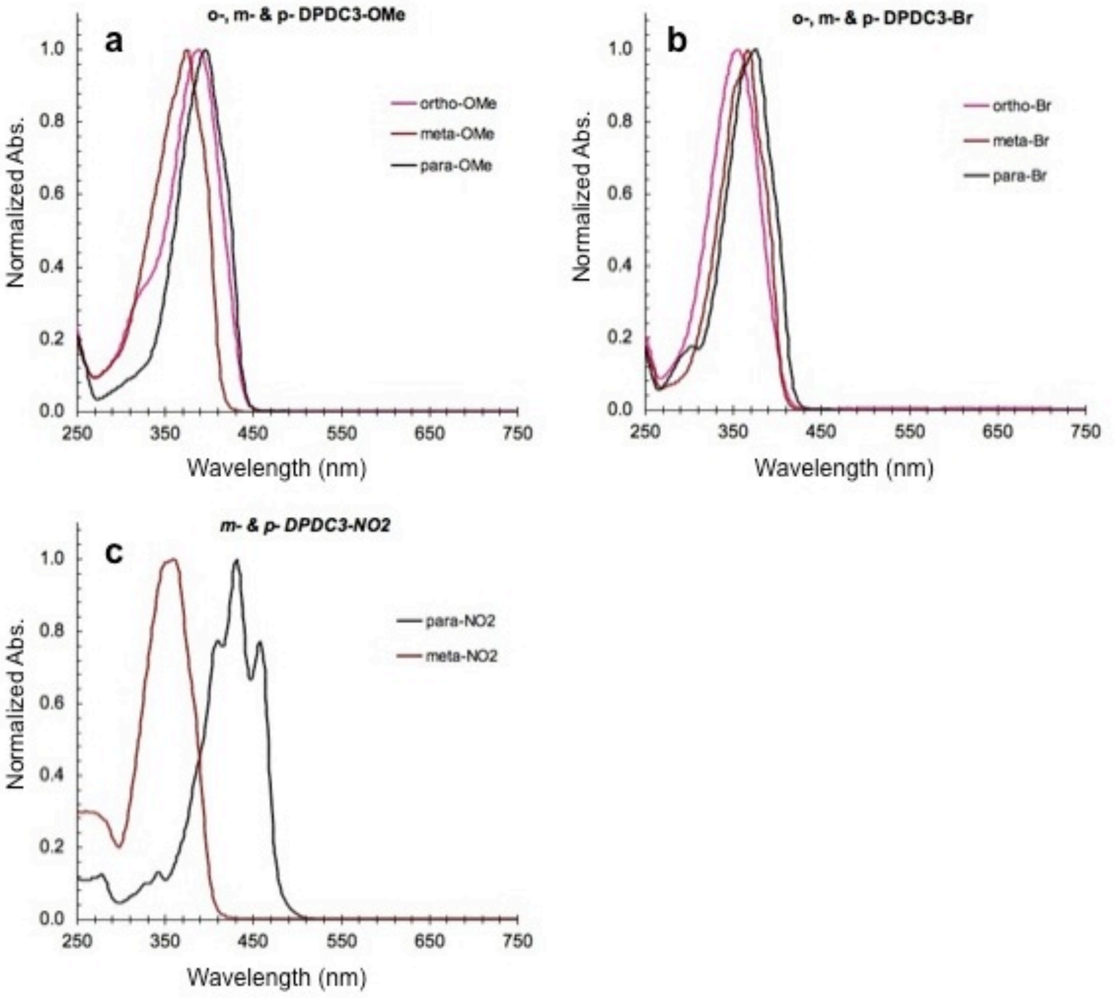


Figure S4. Effects on the substitution pattern of electron-donating and electron-withdrawing groups were investigated. UV-Vis absorption spectra (a) **DPDC3-OMe**, (b) **DPDC3-Br** and (c) **DPDC3-NO$_2$** derivatives were taken in dichloromethane solutions. Our observations agree well with Hammett coefficients suggesting that *para*-substitutions are most strongly coupled to the π-conjugated oligoene backbone.

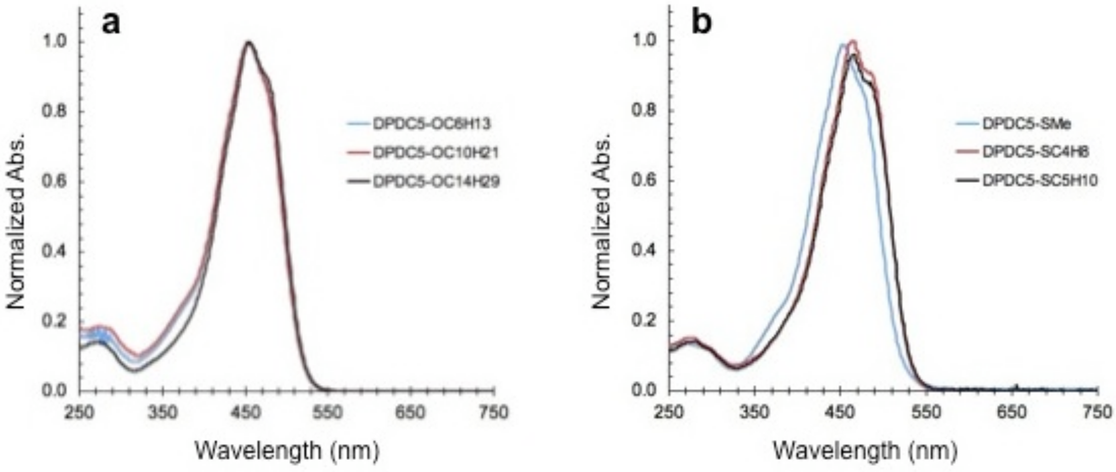


Figure S5. The physical properties can be tuned independently from the electronic structure as shown in the following collections of **DPDC5** derivatives: (a) **DPDC5-OC$_6$H$_{13}$**, **DPDC5-OC$_{10}$H$_{21}$**, **DPDC5-OC$_{14}$H$_{29}$**; and (b) **DPDC5-SMe**, **DPDC5-SC$_4$H$_8$**, **DPDC5-SC$_5$H$_{10}$**. Spectra obtained in dichloromethane solutions.

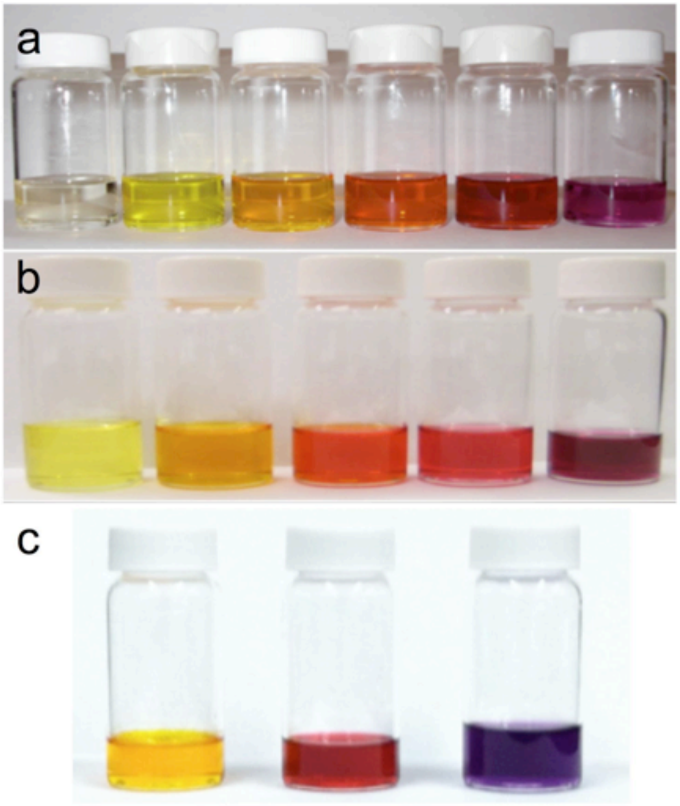


Figure S6. Photograph of dilute solutions (~10^{-4} M) of oligoene series (a) **DPDCn** (b) **DPDCn-SMe** and (c) **DPDCn-NMe$_2$** in dichloromethane.

Extinction Coefficient Values for DPDCn's and Their Derivatives:

Molecule	Wavelength (nm)	Extinction (cm^{-1}*mol^{-1})
DPDC3	353[a]	5.00×10^4
	366	5.44×10^4
	383[a]	3.78×10^4
DPDC5	399[a]	7.51×10^4
	418	1.00×10^5
	442	7.85×10^4
DPDC7	284	1.34×10^4
	438	8.69×10^4
	460	1.16×10^5
	489	1.02×10^5
DPDC9	307	1.54×10^4
	480	9.69×10^4
	498	1.13×10^5
	526	8.40×10^4
DPDC11	330	2.73×10^4
	485[a]	9.36×10^4
	512	1.27×10^5
	540	1.22×10^5
DPDC13[c]	351	3.14×10^4
	510[a]	9.45×10^4
	536	1.24×10^5
	572	1.09×10^5
DPDC3-SMe	225	1.45×10^4
	412	7.33×10^4
DPDC5-SMe	267	1.18×10^4
	453	8.25×10^4
	476[a]	7.11×10^4
DPDC7-SMe	263	1.44×10^4
	309	1.46×10^4
	487	1.04×10^5
	513[a]	8.59×10^4
DPDC9-SMe[c]	308	2.34×10^4
	476[a]	1.22×10^5
	498	1.41×10^5
	526	1.03×10^5
DPDC11-SMe[c]	312[a]	1.93×10^4
	350	2.57×10^4
	497[a]	7.10×10^4
	527	9.00×10^4
	555[a]	8.12×10^4

Molecule	Wavelength (nm)	Extinction (cm^{-1}*mol^{-1})
DPDC3-SC_4H_8	263	3.87 x 10^4
	382	5.62 x 10^4
	485[a]	4.74 x 10^4
DPDC5-SC_4H_8	280	1.41 x 10^4
	463	9.61 x 10^4
	485[a]	8.57 x 10^4
DPDC7-SC_4H_8	274	5.38 x 10^4
	497	1.24 x 10^5
	525[a]	1.03 x 10^5
DPDC9-SC_4H_8	336	2.23 x 10^4
	523	1.07 x 10^5
	552[a]	8.82 x 10^4
DPDC11-SC_4H_8	353	2.52 x 10^4
	359	2.52 x 10^4
	537	1.22 x 10^5
	557	1.18 x 10^5
DPDC3-SC_5H_{10}	264	1.19 x 10^4
	424	6.72 x 10^4
	447[a]	5.29 x 10^4
DPDC5-SC_5H_{10}	280	1.18 x 10^4
	463	7.62 x 10^4
	484[a]	6.91 x 10^4
DPDC7-SC_5H_{10}	271	1.41 x 10^4
	317	1.32 x 10^4
	498	1.04 x 10^5
	526[a]	8.75 x 10^4
DPDC9-SC_5H_{10}	284	1.27 x 10^4
	339	1.38 x 10^4
	526	9.23 x 10^4
	555[a]	7.71 x 10^4
DPDC11-SC_5H_{10}	353	2.50 x 10^4
	360	2.54 x 10^4
	539	1.28 x 10^5
	558[a]	1.26 x 10^5
DPDC13-SC_5H_{10}	336	2.39 x 10^4
	375	3.12 x 10^4
	658	1.27 x 10^5
	589[a]	1.13 x 10^5

Molecule	Wavelength (nm)	Extinction (cm^{-1}*mol^{-1})
DPDC3-NMe$_2$	264	6.82×10^3
	383[a]	3.55×10^4
	464	3.19×10^4
	485[a]	7.38×10^3
DPDC5-NMe$_2$	264	1.33×10^4
	325	1.14×10^4
	521	8.82×10^4
DPDC7-NMe$_2$	328	1.25×10^4
	426[a]	2.26×10^4
	521	9.09×10^4
DPDC3-NPh$_2$	303	2.03×10^4
	476	4.84×10^4
DPDC5-NPh$_2$	306	2.80×10^4
	516	8.45×10^4
DPDC3-Br	242	1.08×10^4
	359[a]	5.59×10^4
	377	6.49×10^4
	396[a]	4.31×10^4
DPDC5-Br	258	1.37×10^4
	404[a]	7.67×10^4
	425	1.03×10^5
	450	8.00×10^4
DPDC7-Br	290	1.46×10^4
	371[a]	1.32×10^4
	441	7.58×10^4
	463	9.88×10^4
	492	7.76×10^4
DPDC9-Br[c]	311	1.24×10^4
	477[a]	6.01×10^4
	501	6.98×10^4
	529	5.08×10^4
DPDC3-CO$_2$H[b]	368[a]	5.13×10^4
	383	5.60×10^4
	404[a]	3.62×10^4
DPDC5-CO$_2$H[b]	343[a]	6.16×10^3
	384[a]	1.91×10^4
	411[a]	3.90×10^4
	434	5.17×10^4
	460	4.06×10^4

Molecule	Wavelength (nm)	Extinction (cm^{-1}*mol^{-1})
DPDC7-CO_2H[b]	296	1.27×10^4
	450	4.84×10^4
	474	6.19×10^4
	505	4.93×10^4
DPDC3-CO_2Et	362[a]	5.70×10^4
	378	6.18×10^4
	398[a]	3.94×10^4
DPDC5-CO_2Et	266	1.37×10^4
	337	1.38×10^4
	405	8.24×10^4
	427	1.10×10^5
	453	8.48×10^4
DPDC7-CO_2Et[c]	295	8.94×10^3
	370	9.18×10^3
	441	4.32×10^4
	465	5.68×10^4
	496	4.43×10^4
DPDC3-OC_6H_{13}	258	1.33×10^4
	411	6.40×10^4
	432[a]	5.03×10^4
DPDC5-OC_6H_{13}	276	9.53×10^3
	427[a]	5.27×10^4
	454	7.50×10^4
	476[a]	6.69×10^4
DPDC7-OC_6H_{13}	271	9.73×10^3
	305	9.20×10^3
	493	8.58×10^4
	521[a]	7.10×10^4
DPDC3-$OC_{10}H_{21}$	247	1.47×10^4
	411	3.47×10^4
	431[a]	2.73×10^4
DPDC5-$OC_{10}H_{21}$	278	1.38×10^4
	454	8.20×10^4
	474[a]	7.28×10^4
DPDC7-$OC_{10}H_{21}$	300	1.45×10^4
	492	4.96×10^4
	519[a]	4.14×10^4
DPDC3-C_8H_{13}	249	1.37×10^4
	379[a]	5.85×10^4
	399	7.16×10^4
	423[a]	4.64×10^4

Molecule	Wavelength (nm)	Extinction (cm^{-1}*mol^{-1})
DPDC5-C_8H_{13}	279	1.34 x 10^4
	420[a]	6.89 x 10^4
	443	9.08 x 10^4
	470	6.97 x 10^4
DPDC7-C_8H_{13}	303	2.36 x 10^4
	453[a]	1.10 x 10^5
	478	1.43 x 10^5
	508	1.13 x 10^5
DPDC3-CN	238	1.34 x 10^4
	361[a]	5.29 x 10^4
	376	5.68 x 10^4
	395[a]	3.74 x 10^4
DPDC5-CN	264	1.51 x 10^4
	402	7.61 x 10^4
	424	1.03 x 10^5
	450	8.12 x 10^4
***ortho*-DPDC3-Br**	230	9.26 x 10^3
	355	3.79 x 10^4
***meta*-DPDC3-Br**	240	9.92 x 10^3
	352[a]	4.96 x 10^4
	367	5.52 x 10^4
	385[a]	3.66 x 10^4
***ortho*-DPDC3-OMe**	242	8.57 x 10^3
	321[a]	1.10 x 10^4
	389	3.60 x 10^4
***meta*-DPDC3-OMe**	229	1.20 x 10^4
	374	4.76 x 10^4
***para*-DPDC3-OMe**	249	1.14 x 10^4
	396	5.72 x 10^4
***meta*-DPDC3-NO_2**[c]	281	1.81 x 10^3
	359	3.09 x 10^3
DPDC3-NO_2	236	7.29 x 10^3
	267	6.69 x 10^3
	390	4.59 x 10^4
	414[a]	2.89 x 10^4
DPDC5-NO_2	228	3.21 x 10^4
	415[a]	5.20 x 10^4
	437	6.77 x 10^4
	462	5.20 x 10^4

Molecule	**Wavelength (nm)**	**Extinction (cm^{-1}*mol^{-1})**
DPDC3-F	236	1.18 x 10^{4}
	367	5.60 x 10^{4}
	382[a]	4.27 x 10^{4}

Table S1. UV-vis spectra were obtained in dichloromethane solutions. [a]Peaks were not well-defined; absorption shoulder. [b]Spectra were obtained in DMSO due to limited solubility. [c]There is more error in these values due to their extreme insolubility.

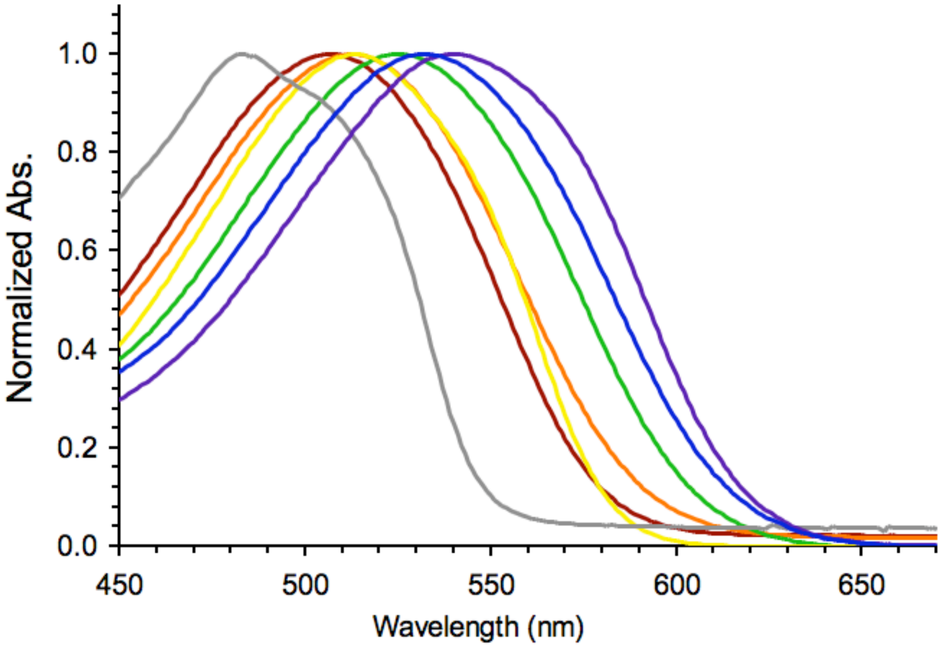


Figure S7. Salvotochromic behavior of **DPDC5-NMe$_2$** selected solvents; heptane (grey) ethyl acetate (red), acetone (orange), toluene (yellow), chlorobenzene (green), DMSO (blue), and nitrobenzene (purple). Absorbance is normalized to 1 for clarity. A full list of 15 different solvents is included in Table S1.

#	Solvent	λmax (nm)
1	nitrobenzene	539
2	dimethyl sulfoxide	533
3	1,1',2,2'-Tetrachloroethane	529
4	dimethylformamide	523
5	chlorobenzene	523
6	methylene chloride	520
7	chloroform	518
8	tetrahydrofuran	514
9	acetonitrile	512
10	acetone	512
11	benzene	511
12	toluene	511
13	ethyl acetate	506
14	dietheyl ether	500
15	n-heptane	484

Table S2. Solvatochromism survey in the UV-vis absorption maxima for **DPDC-NMe$_2$**.

III. Cyclic Voltammetry.

General Procedure and Data Analysis: Cyclic voltammetry (CV) was preformed using a CHI600c potentiometer. All electrodes were purchased from Bioanalytical Systems, Inc; working electrode was a glass carbon electrode (MF-2070), reference electrode was Ag/AgCl (MF-2062), and auxiliary electrode was a platinum electrode (MW-4130). All measurements were carried out under argon in dimethylformamide (DMF) solution with tetrabutylammonium hexafluorophosphate electrolyte (0.1 M) and oligoene (350 μM). Ferrocene was used as an internal standard. To assure that the addition of the internal standard did not affect the redox chemistry of the analyte, oligoene solutions were first measured without the presence of ferrocene and then again with the internal standard. Ionization potentials were then set relative to that of ferrocene at E^0 = -4.8 eV.

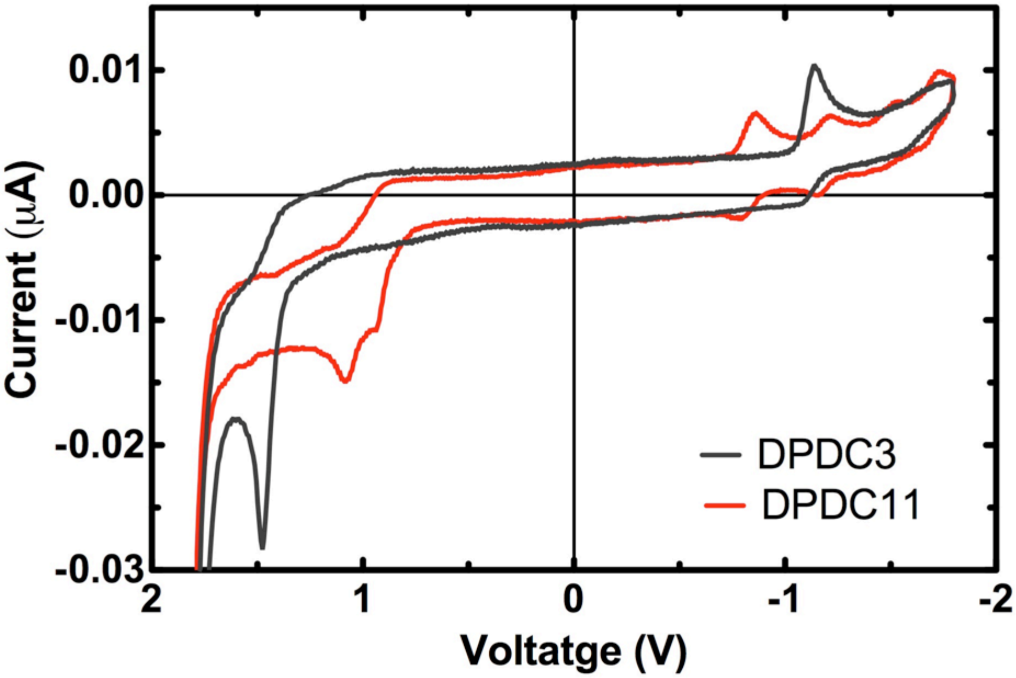


Figure S8. Comparison of ionization potentials obtained from cyclic voltammetry (CV). As a general trend, reductions become more reversible as the molecular length increases. Oxidations, on the other hand, are generally unstable, where apparent deposition of the oxidized material is observed on the electrode surface. The irreversibility of the oxidations does not change if the CV was stopped before reaching the solvent oxidation. Ferrocene was used as an internal standard.

Tabulated DPDCn Redox Potentials:

Molecule	**Reductions**								**Oxidations**			
	E_1	$E^0{}_1$	E_2	$E^0{}_2$	E_3	$E^0{}_3$	E_4	$E^0{}_4$	E_1	$E^0{}_1$	E_2	$E^0{}_2$
DPDC3	-3.09	-3.13	-	-	-	-	-	-	-5.74	-	-	-
DPDC5	-3.25	-3.28	-	-	-	-	-	-	-5.47	-	-	-
DPDC7	-3.29	-3.34	-2.85	-2.90	-2.51	-	-	-	-5.32	-	-5.57	-
DPDC9	-3.33	-3.38	-2.97	-3.02	-2.90	-2.76	-	-	-5.25	-	-5.42	-
DPDC11	-3.37	-3.43	-3.03	-3.07	-2.97	-2.84	-2.49	-	-5.19	-	-5.34	-
DPDC13	-3.38	-3.44	-3.06	-3.11	-3.06	-2.94	-2.59	-	-5.14	-	-5.27	-

Table S3. Ionization potentials obtained by CV. Oligoene solutions (350 μM) were prepared in DMF with tetrabutylammonium hexafluorophosphate electrolyte (0.1 M). All value are relative to ferrocene (E^0 = -4.8 eV) as internal standard.

DPDCn	**DPDC3**	**DPDC5**	**DPDC7**	**DPDC9**	**DPDC11**	**DPDC13**
LUMO	-3.125	-3.275	-3.335	-3.375	-3.425	-3.435
HOMO	-5.740	-5.470	-5.320	-5.250	-5.190	-5.140
DPOn	**DPO3**	**DPO5**	**DPO7**			
LUMO	-2.448	-2.650	-2.770			
HOMO	-5.298	-5.193	-4.969			
Difference in LUMO	0.677	0.625	0.565			
Difference in HOMO	0.442	0.277	0.351			

Table S4. Redox potentials estimate the HOMO and LUMO energy differences between series **DPDCn** and **DPOn**. The installation of nitriles lowers the energy of both the LUMO (up to 0.68 eV) and the HOMO (up to 0.44 eV) and shrinks the molecular band gap, E_{cv}, as much as 0.24 eV. Longer **DPOn** oligomers could not be synthesized/characterized due to their high insolubility.

IV. Particle in a Box Model for Electron Confinement in DPDCn Series.

As a simple model for small-scale confinement, the energies of a one-dimensional "particle in a box" were found to relate the optical absorptions and electrochemical redox potential gaps, E_{cv}, of the **DPDCn** series.

$$E_n = \frac{n^2\hbar^2\pi^2}{2m^*L^2} = \frac{n^2h^2}{8m^*L^2}$$

Where L is the molecular length, which was obtained directly from the crystal structures and measured between the *para*-positioned hydrogens at each end of the molecule (see Table S5). The strongest wavelength absorption (λ_{max}), solution optical band gap (E_{og}), and the electrochemical band gap (E_{CV}) can be described with this model. Linear regression analysis yielded fitted lines with R^2 values > 0.99. Simple extrapolative analysis to oligomers of infinite lengths predicts values that agree well with those obtained experimentally for the polymer, polyacetylene.

L (nm)	$1/L^2$ (nm^{-2})	λ_{max} (eV)	E_{OG} (eV)	E_{CV} (eV)
1.633	0.3752	3.39	2.86	2.62
2.104	0.2259	2.97	2.42	2.20
2.591	0.1490	2.70	2.13	1.99
3.077	0.1056	2.49	1.97	1.88
3.555	0.0791	2.42	1.86	1.77
4.043	0.0612	2.31	1.76	1.71
Extrapolation Results				
slope	n/a	3.40	3.47	2.86
y-intercept	n/a	2.15	1.59	1.55

Table S5. Values used for particle in a box modeling of **DPDCn** series. Molecular length (L) was obtained from crystal structures and measured between the *para*-positioned carbons at each end of the molecule. The values for the slope and y-intercept obtained from our simple extrapolative analysis are also tabulated.

In order to calculate the resulting effective mass, data was converted to standard units of energy (erg), time (s), mass (g) and length (cm). Given the equation above the slope obtained from our linear regression would have units [erg x s].

$$slope = \frac{h^2}{8m^*}$$

Thus, the appropriate value for Planck's constant was chosen, 6.626 x 10^{-27} erg x s, providing mass in grams.

$$[erg] \times [cm^2] = \frac{[erg \times s]^2}{m^*}$$

$$[erg] = \frac{[g \times cm^2]}{s^2}$$

$$m^* = [g]$$

A sample calculation gives an effective mass; To a fi.st order approximation the exciton behaves as a spatially confined quantum mechanical particle relative to the length of the molecule.

$$m^* = \frac{h^2}{8 \times (slope)}$$

$$m^* = \frac{(6.626 \times 10^{-27} erg \cdot s)^2}{8 \cdot (2.551 \times 10^{-12} erg \times cm^2)} = 2.151 \times 10^{-42} g = 2.151 \times 10^{-45} kg$$

V. Crystal Structures.

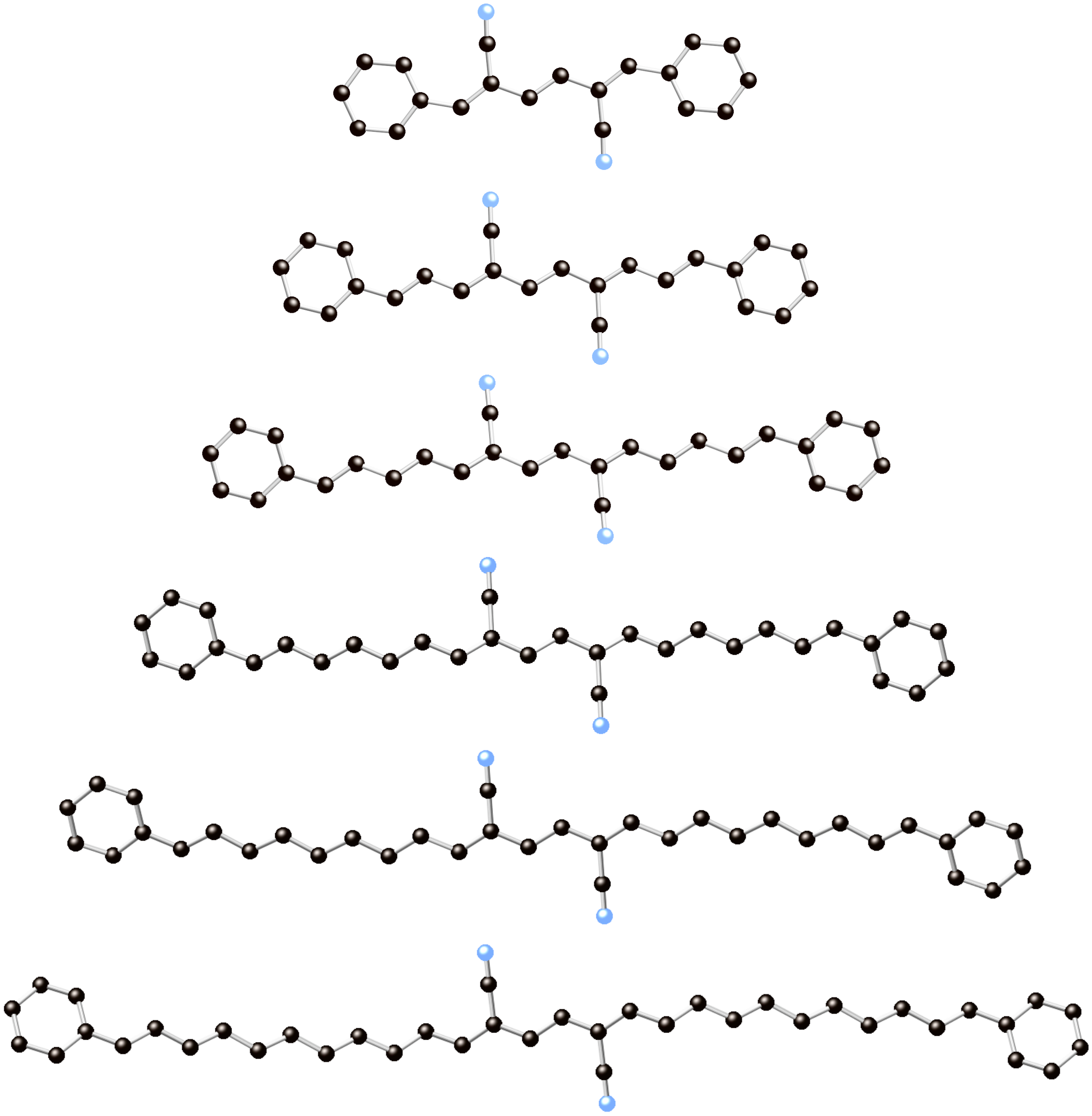


Figure S9. Crystal structures of **DPDCn** series were determined by single crystal X-ray diffraction.

Figure S10. Packing structures of **DPDC3**, **DPDC7**, **DPDC9** and **DPDC11** (left to right). Solid-state packing changes from herringbone-type to aligned stacks of oligoenes as oligoene length is increased.

VI. Nanoparticle Synthesis and SAM preparation.

General information. Gallium Arsenide (100) single crystalline wafer was purchased from Sigma-Aldrich. Ammonium Hydroxide, 30% in water (NH_4OH) and Ethanol, 200 proof (EtOH) were purchased from Fischer Scientific. Dimethyl Sulfoxide (DMSO) 99% anhydrous was purchased from Sigma-Aldrich. EtOH and DMSO were degassed over several (three or greater) freeze pump thaw cycles before use. Iron (III) chloride 97%, and oleic acid 90% were purchased from Sigma-Aldrich. Sodium oleate 97% was purchased from TCI. 1-octadecene 90% was purchased from Acros Organics. Hexane was purchased from Fischer Scientific. Monolayer formation was observed using a Hitachi S-4700 FE-SEM.

Nanoparticle Synthesis. Fe_3O_4 nanoparticles were prepared using the method developed by Hyeon *et al.*[19] Iron oleate precursor was made by adding 10.8 g of iron (III) chloride and 36.5 g of sodium oleate into a mixed solvent of 30 mL of ethanol, 40 mL of DI water and 70 mL of hexane. The reaction was kept at 60 ºC for 4 hours and the product was purified with DI water and then dried under vacuum. The 10 nm Fe_3O_4 nanoparticles were synthesized by mixing 3.6 g of iron oleate, 1.28 mL of oleic acid and 20 mL of 1-octadecene into a three neck flask, and the solution was heated to 320 ºC at a heating rate of 200 ºC/hr and kept at 320 ºC for 30 minutes. After the reaction mixture was cooled to room temperature, ethanol was added as anti-solvent to precipitate the nanoparticles by centrifugation. The precipitated nanoparticles were re-dispersed in hexane.

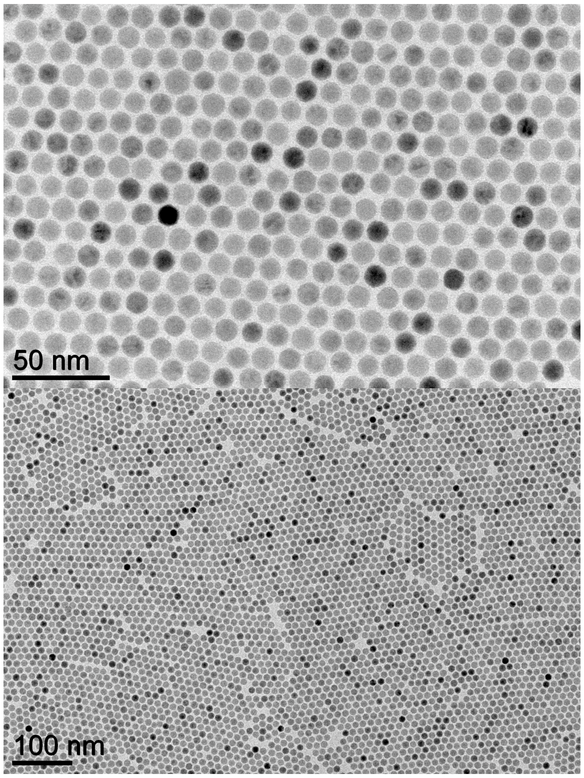


Figure S11. TEM images of as-synthesized 10-nm Fe_3O_4 nanoparticles.

Monolayer Formation Procedure. Gallium Arsenide crystal was cut into several 0.75-1.0 cm square wafers using a diamond scribe. The wafers were submerged in NH_4OH and allowed to stand covered for 10 minutes. Upon removal from the NH_4OH, a wafer is rinsed with ethanol, dried under an argon stream, rinsed and dried a second time, them immediately submerged in a 1.5 mM solution of **DPDC3-CO$_2$H** in dimethyl sulfoxide (DMSO). The solution is transferred to a nitrogen glove box and allowed to stand for 16 hours. After removal from the glove box, the wafer is removed from the solution, rinsed thoroughly with ethanol and dried under an argon stream. It is immediately submerged into a solution of 10-nm iron oxide (Fe_3O_4) nanoparticles in dimethylformamide, and allowed to stand 1-2 hours. Upon removal from the nanoparticle solution, the wafer is rinsed with ethanol and dried under an argon stream, at which point they are ready for microscopy (Figure S12a).

Controls. In order to probe the dependence of monolayer formation on oligoene concentration in DMSO, the above procedure was carried out using both 3.0 and 6.0 mM solutions. It was found that nanoparticle coverage increased with increasing concentration of **DPDC3-CO$_2$H** (Figure S12b and S12c).

We verified that monolayer formation is initiated by the oligoene connectors. Two controls were carried out: First, to eliminate the possibility that DMSO was acting as a inter-particle connector the above procedure was carried out using pure DMSO in place of the oligoene solution; secondly, in order to eliminate the possibility that submersion into the nanoparticle solution was sufficient to generate monolayers, a wafer was placed into the nanoparticle solution directly after cleaning. No monolayer formation was observed in either case as seen in Figure S12c and S12d.

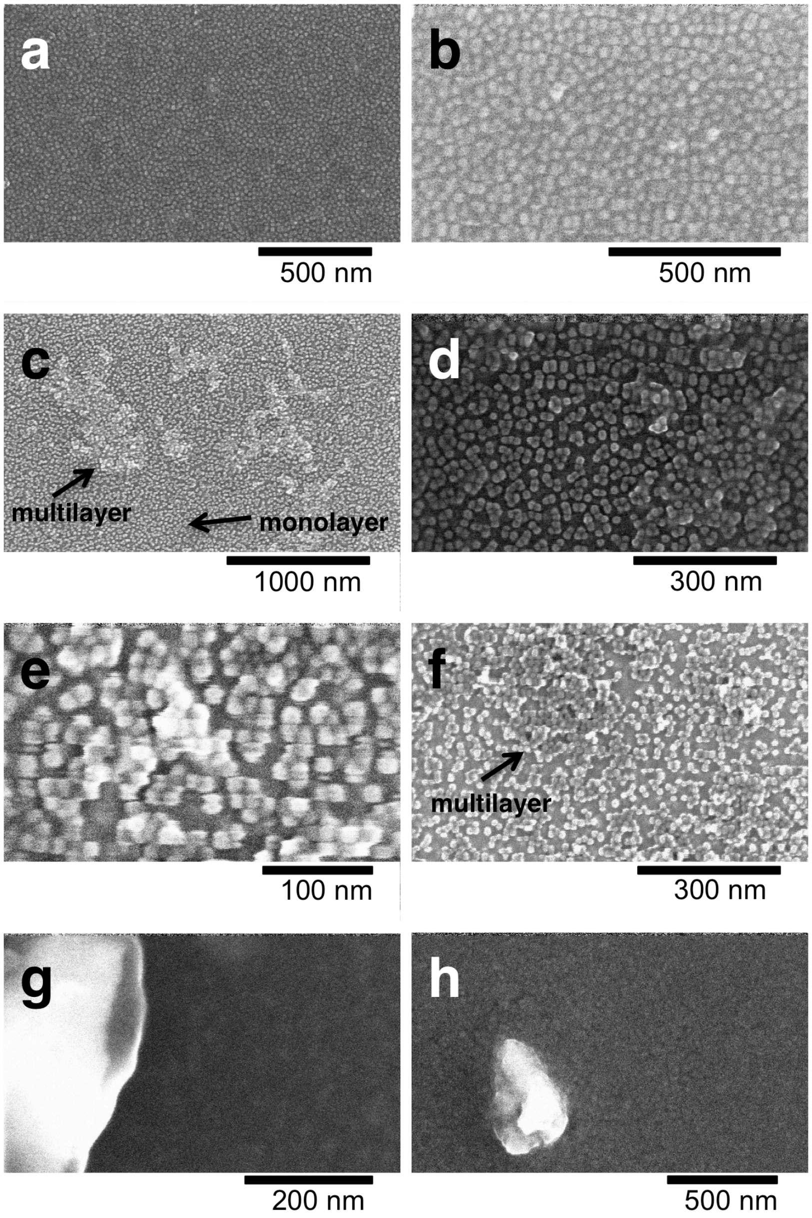


Figure S12. SEM images of monolayers of Fe_3O_4 nanoparticles formed after carrying out the above procedure using: (a) 1.5 mM **DPDC3-CO_2H,** where the scale bar represents a distance of 500 nm; (b) 1.5 mM **DPDC3-CO_2H,** where the scale bar represents a distance of 300 nm; (c) 3.0 mM **DPDC3-CO_2H,** where the scale bar represents a distance of 1 μm; (d) 3.0 mM **DPDC3-CO_2H,** where the scale bar represents a distance of 300 nm; (e) 6.0 mM **DPDC3-CO_2H,** where the scale bar represents a distance of 100 nm; (f) 6.0 mM **DPDC3-CO_2H,** where the scale bar represents a distance of at 300 nm; (g) DMSO only; (h) DMF only.

VI. Theoretical Methods and Details.

All electronic structure calculations used Jaguar (version 7.0, Schrodinger LLC, New York, NY, 2007) using the B3LYP hybrid functional and the 6-31G** basis sets. The geometries of **DPDCn** and **DPOn** were fully optimized. The final geometries, total energies, bond angles and bond distances can be found in a separate supporting information file. Below is a summary the results of our calculations on selected **DPDC5** and **DPO5** derivatives.

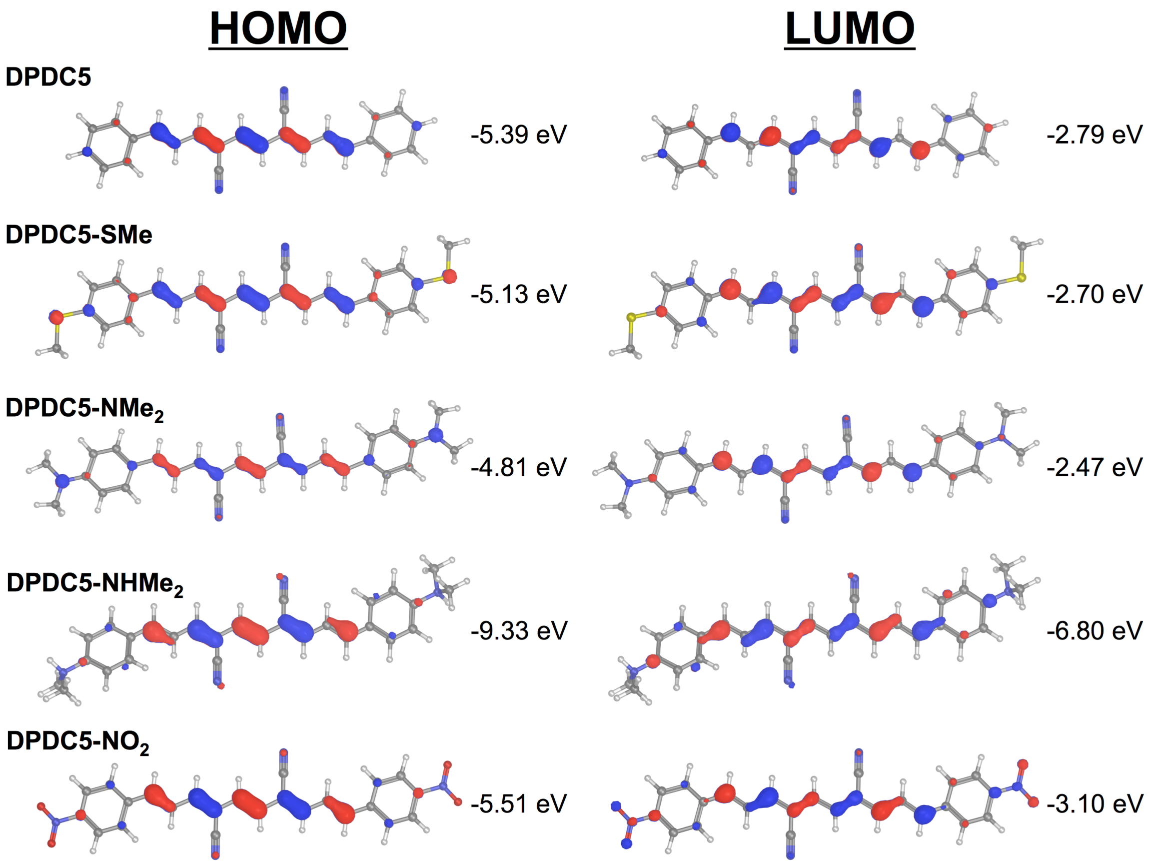


Figure S13. HOMO and LUMO topologies of selected **DPDC5** derivatives predicted by DFT B3LYP 6-31G** (gas phase).

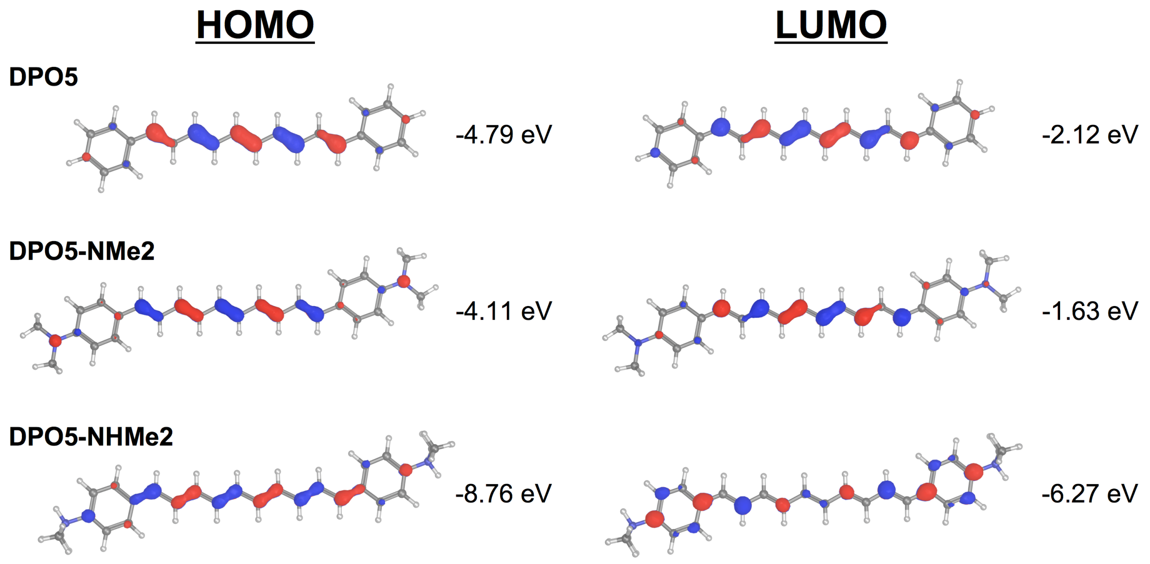


Figure S14. HOMO and LUMO topologies of selected **DPO5** derivatives predicted by DFT B3LYP 6-31G** (gas phase).

VIII. Comparison of DPDCn Band Gaps from Various Methods

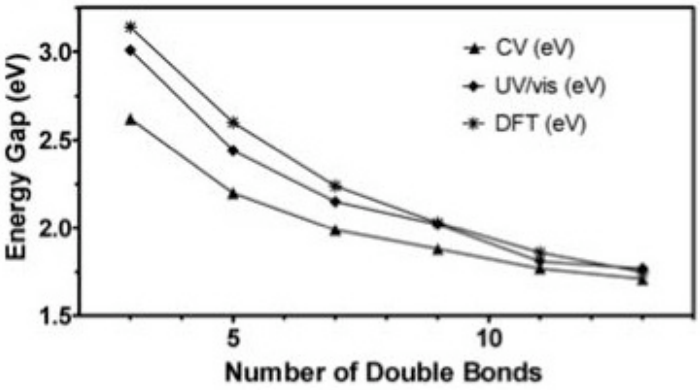


Figure S15. Comparison of band gap estimations from CV, UV-Vis and DFT.

# of Double Bonds	UV-Vis Eg (eV)†	CV Eg (eV)	DFT (eV)
3	3.01	2.62	3.14
5	2.44	2.20	2.60
7	2.15	1.99	2.24
9	2.02	1.88	2.03
11	1.81	1.77	1.86
13	1.77	1.71	1.75

Table S6. Bad Gap Estimations from various methods.

IX. References.

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