Sequence Matters: Modulating Electronic and Optical Properties of

Conjugated Oligomers via Tailored Sequence.

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SYNTHETIC SCHEMES FOR MONOMERS





Scheme S2. Synthesis of P-A-CN (3).



Scheme S3. Synthesis of P-B-CN (4).



GENERAL METHODS¹

Materials. Anhydrous DMF, "BuLi (1.6 M in hexanes), and DIBAL-H (1.0 M in hexanes) were purchased from Aldrich and dispensed using air-sensitive techniques. Benzoyl peroxide and NBS were stored at -20 °C. KO'Bu was stored in a desiccator over anhydrous CaSO₄. LiCl was dried at 120 °C for at least 24 h. Anhydrous diethyl ether for lithiation reactions was opened immediately prior to use. Reagent grade THF was used for most reactions; notably the HWE reactions used reagent grade THF. DCM for reactions was dried by refluxing with CaH₂. 1,6-

¹ The general methods section is also found in the paper and is reproduced here for ease of interpreting the experimentals that follow.

Bis(hexyloxy)benzene (5) was prepared as previously reported.¹ All other reagents (including compounds 7 and 8) and solvents were used as received. Column chromatography was carried out on standard grade silica gel (60 Å pore size, 40-63 μ m particle size), which was purchased and used as received. Hexanes, dichloromethane, and ethyl acetate used for column chromatography were purchased and used as received. Melting points for all compounds were determined by DSC and are found in the main text in Table 2, listed as T_{iso}.

NMR Spectroscopy. ¹H (300 and 400 MHz) and ¹³C (75, 100 and 150 MHz) NMR spectra were recorded on Bruker spectrometers. Chemical shifts were referenced to residual ¹H or ¹³C signals in deuterated solvents (7.27 and 77.0 ppm, respectively, for CHCl₃ and 5.32 and 54.0 ppm, respectively, for CH₂Cl₂).

Mass Spectrometry. HRMS were recorded on EI-quadrupole or ESI-TOF instruments in the Mass Spectrometry Facility of the University of Pittsburgh.

Optical Spectroscopy. UV/VIS absorption spectra were recorded in CHCl₃ on a Perkin Elmer Lambda 9 UV/VIS/NIR spectrometer. Solution (CHCl₃) and film emission spectra were recorded on a Varian Cary Eclipse fluorimeter. Films were drop cast on quartz slides from CHCl₃.

Thermal Analysis. DSC was performed on a Perkin Elmer Pyris 6 with a heating and cooling rate of 10 °C/min.

Electrochemistry. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed on a CHI Electrochemical Workstation Model 430a (Austin, TX) collected using a three electrode system consisting of a glassy carbon disk (3 mm dia.) as working electrode, a non-aqueous Ag/Ag+ reference electrode (1 mM $AgNO_3$ in acetonitrile), and a Pt-wire as auxiliary electrode in 0.1 M Bu₄NPF₆ in THF freshly distilled from sodium. CV were recorded at

100 mV/s. DPV parameters were as follows: scan rate of 25 mV/s, pulse amplitude 0.05 V and pulse period 0.16 s.

SYNTHESIS OF MONOMERS

Although some of the starting materials and a selection of the oligomers have been previously reported by others, the exact synthesis used and characterization data for all compounds is included herein.



1,4-dibromo-2,5-bis(hexyloxy)benzene (6). This compound has been previously synthesized using a procedure in CCl_{4} ,² which we were unwilling to handle and unable to acquire in the amounts necessary for our needs. A new procedure using methanol is described. Bromine (70.0 mL, 1.36 mol) was added dropwise to methanol (650 mL) at 0° C. **5** (75.0 g, 269 mmol) was added and the mixture was refluxed for 48 h. The reaction mixture was extracted with hexanes (4x 250 mL). The combined organic layers were washed with 20% aq. NaHSO₃ (2x 200 mL), water (200 mL), and brine (200 mL). The solution was dried over MgSO₄, and the solvent was removed in vacuo. The residue was recrystallized (9:1 methanol:CH₂Cl₂) to give the title compound as a white solid (88.5 g, 75%). ¹H NMR (CDCl₃, 300 MHz) δ 0.93 (6H, t, J = 6.8 Hz), 1.30-1.40 (8H, mult), 1.40-1.55 (4H, mult), 1.81 (4H, tt J = 6.8, 6.4 Hz), 3.95 (4H, t, J = 6.4 Hz),

7.09 (2H, s) ppm. ¹³C NMR (CDCl₃) δ 14.00 (CH₃), 22.56 (CH₂), 25.59 (CH₂), 29.06 (CH₂),
31.46 (CH₂), 70.26 (OCH₂), 111.09 (ArBr quat), 118.41 (Ar CH), 150.04 (ArO quat) ppm.
HRMS calcd. for C₁₈H₂₈O₂Br₂: 434.0456 g/mol. Found: 434.0450 g/mol.

4-bromo-2,5-bis(hexyloxy)benzaldehyde (2 or Br-B-CHO). This compound has been previously reported, but the described synthesis by Li, *et al.*,³ was unsuitable for scale-up. We modified the methods of Peng, et al.,⁴ which were used to produce a similar compound. Two batches of 6 (34.9 g, 80.0 mmol each) were each dissolved in Et₂O (150 mL) and cooled to 0 °C under N₂. ⁿBuLi (1.6 M in hexanes, 50 mL, 80 mmol) diluted with 100 mL Et₂O was added to each batch dropwise over 30 min. Anhydrous DMF (10.0 mL, 130 mmol) in Et₂O (35 mL) was added rapidly to each batch. The mixtures were removed from the cold bath and stirred at room temperature for 2 h. The reactions were quenched into water (300 mL). The aqueous layers were extracted with ether (3x100 mL). The organic layers were washed with brine (100 mL) and dried over MgSO₄. The solvent was removed *in vacuo*. The residues of both batches were combined and recrystallized from hexanes and then methanol to give the title compound as a while solid (40.5 g, 66%). ¹H NMR (CDCl₃, 300 MHz) δ 0.80-0.95 (6H,mult), 1.30-1.40 (8H, mult), 1.40-1.55 (4H, mult), 1.75-1.90 (mult, 4H), 4.00 (2H, t, J = 6.4 Hz), 4.02 (2H, t, J = 6.4 Hz), 7.22 (1H, s), 7.30 (1H, s), 10.41 (1H, s) ppm. ¹³CNMR (CDCl₃) & 13.95 (CH₃), 13.97 (CH₃), 22.51 (CH₂), 22.53 (CH₂), 25.57 (CH₂), 25.62 (CH₂), 28.94 (CH₂), 28.98 (CH₂), 31.42 (CH₂), 69.76 (OCH₂), 69.76 (OCH₂), 110.52 (Ar CH), 118.39 (Ar CH), 120.89 (ArBr quat), 124.20 (Ar quat), 149.80

(ArO quat), 155.71 (ArO quat), 188.86 (CHO) ppm. HRMS calcd. for C₁₉H₂₉O₃Br: 384.1300 g/mol. Found: 384.1298 g/mol

4-(dimethoxyphosphorylmethyl)benzonitrile (3 or P-A-CN). p-Tolunitrile (7) (25.0 mL, 209 mmol) was added to 1,2-dicloroethane (400 mL) in a round-bottom flask with stirring. NBS (18.8 g, 105 mmol), and benzoyl peroxide (2.55 g, 10.5 mmol) were added, and the mixture was refluxed until the orange color disappeared (1.5 h). NBS (18.8 g, 105 mmol), and benzoyl peroxide (2.55 g, 10.5 mmol) were added, and the mixture was refluxed again for 1.5 h. The reaction mixture was allowed to stand overnight. The succinimide precipitate was removed by filtration. The filtrate was washed successively with water (200 mL), sat. aq. NaHCO₃ (200 mL), and brine (200 mL). The organic solution was dried over MgSO₄, and the solvent was removed in vacuo. The crude product was dissolved in toluene (100 mL). Trimethyl phosphite (60.0 mL, 508 mmol) was added, and the mixture was refluxed overnight. The solvent was removed in vacuo, and the crude product was purified by column chromatography (silica gel, 4:1 CH₂Cl₂:acetone) and then by recrystallization (1:1 ethyl acetate:hexanes) to give the title compound as an off-white crystalline solid (16.7 g, 35% over 2 steps). MP 79.0-81.0 °C. ¹H NMR (CDCl₃) δ 3.17 (2H, d, ²J_{H-P} = 22.4), 3.66 (6H, d, ³J_{H-P} = 11.2 Hz), 7.37 (2H, dd, J_{H-H} = 8.4 Hz, $J_{H-P} = 2.0$ Hz), 7.58 (d, 2H, $J_{H-H} = 8.0$ Hz) ppm. ¹³CNMR (CDCl₃, 300 MHz) δ 32.92 (d, ¹J_{C-P}) = 137 Hz, CH₂), 52.82 (d, ${}^{2}J_{C-P}$ = 7 Hz, OCH₃), 110.84 (d, ${}^{5}J_{C-P}$ = 3 Hz, Ar guat), 118.45 (d, ${}^{6}J_{C-P}$ = 2 Hz, CN), 130.31 (d, ${}^{3}J_{C-P}$ = 6 Hz, Ar CH), 132.14 (d, ${}^{4}J_{C-P}$ = 3 Hz, Ar CH), 137.02 (d, ${}^{2}J_{C-P}$ =

10 Hz, Ar quat) ppm. MS (EI) 225 (M⁺), 129, 116, 109 (base) m/z. HRMS calcd for $C_{10}H_{12}NO_3P$: 225.0556 g/mol. Found: 225.0555 g/mol.



2-methyl-1,4-bis(hexyloxy)benzene (9). Based on our previous methods,¹ KOH (40.0 g, 713 mmol) and Na₂S₂O₃ (86.0 g, 346 mmol) were dissolved in water (200 mL) in a 1 L round-bottom flask and cooled on ice. 2-Methylhydroquinone (8) (42.8 g, 345 mmol), TBAB (5.0 g, 16 mmol), 1-bromohexane (100 mL, 712 mmol), and PhMe (100 mL) were added the order listed. The mixture was refluxed with vigorous stirring for 40 h. The aqueous layer was extracted with PhMe (2x 100 mL). The combined organic layers were washed with water (100 mL) and brine (100 mL) and dried over MgSO₄. The solvent was removed *in vacuo*. The residue was purified by column chromatography (silica gel, 17:3 hexanes: CH_2Cl_2) to give the title compound as a yellow liquid (86.3 g, 86%). ¹H NMR (CDCl₃) δ 0.90-1.00 (6H, mult), 1.30-1.45 (8H, mult), 1.45-1.60 (4H, mult), 1.75-1.90 (4H, mult), 3.94 (2H, t, J = 6.4 Hz), 3.95 (2H, t, J = 6.4 Hz), 6.71 (1H, dd, J = 9.0 Hz, 3.0 Hz), 6.77 (1H, d, J = 9.0 Hz), 6.79 (1H, d, J = 3.0 Hz) ppm. ¹³C NMR (CDCl₃) & 13.99 (CH₃), 16.34 (CH₃), 22.60 (CH₂), 25.75 (CH₂), 25.83 (CH₂), 29.39 (CH₂), 29.45 (CH₂), 31.59 (CH₂), 31.61 (CH₂), 68.41 (OCH₂), 68.68 (OCH₂), 111.46 (Ar CH), 112.11 (Ar CH), 117.56 (Ar CH), 128 (Ar quat), 151.39 (ArO quat), 152.78 (ArO quat) ppm. MS(EI): 292 (M⁺), 234, 221, 208, 165, 150, 124 (base), 107, 95, 84, 77, 67, 55 m/z. HRMS calcd for C₁₉H₃₂O₂: 292.2402 g/mol. Found: 292.2406 g/mol.



1-bromo-2,5-bis(hexyloxy)-4-methylbenzene (10). 9 (37.5 g, 128 mmol) was dissolved in 1,2dichloroethane (375 mL). NBS (23.0 g, 129 mmol) and benzoyl peroxide (1.56 g, 6.44 mmol) were added and the mixture was refluxed for 5h. Hexanes (100 mL) was added to precipitate succinimide. The filtrate was washed with water (3x 100 mL), sat. aq. NaHCO3 (100 mL), and brine (100 mL). The solution was dried over MgSO4, and the solvent was removed in vacuo. The residue was recrystallized from methanol to give the title compound as a white solid (33.0 g, 69%). ¹H NMR (CDCl₃) δ 0.90-1.00 (6H, mult), 1.30-1.40 (8H, mult), 1.45-155 (4H, mult), 1.75-1.90 (4H, mult), 2.19 (3H, s), 3.90 (2H, t, J = 6.4 Hz), 3.96 (2H, t, J = 6.4 Hz), 6.76 (1H, s), 6.99 (1H, s) ppm. ¹³C NMR (CDCl₃, 300 MHz) δ 13.98 (CH₃), 14.00 (CH₃), 16.22 (CH₃), 22.58 (CH₂), 25.65 (CH₂), 25.74 (CH₂), 29.26 (CH₂), 29.29 (CH₂), 31.52 (CH₂), 68.84 (OCH₂), 70.28 (OCH₂), 108.88 (ArBr quat), 116.28 (Ar CH), 116.90 (Ar CH), 126.28 (Ar quat), 149.15 (ArO quat), 151.72 (ArO quat) ppm. MS (EI): 372 (M⁺²), 370 (M⁺), 288, 286, 204, 202 (base), 164, 124, 94, 84, 77, 69 m/z. HRMS calcd for C₁₉H₃₁O₂Br: 370.1507 g/mol. Found: 370.1500 g/mol.



2,5-bis(hexyloxy)-4-methylbenzaldehyde (11). Based on the methods of Peng, *et al.*,⁴ **10** (30.0 g, 80.1 mmol) was dissolved in Et₂O (150 mL) and cooled to 0 °C under N₂. ⁿBuLi (1.6 M in hexanes, 55 mL, 88 mmol) diluted with 100 mL Et₂O was added dropwise over 30 min. DMF

(10.0 mL, 130 mmol) in Et₂O (35 mL) was added rapidly. The mixture was removed from the cold bath and stirred at room temperature for 2 h. The reaction was quenched by pouring into water (300 mL). The aqueous layer was extracted with ether (3x 100 mL). The organic layers were washed with brine (100 mL) and dried over MgSO₄. The solvent was removed *in vacuo*. The residue was purified by column chromatography (silica gel, 19:1 hexanes:EtOAc) to give the title compound as an off-white solid (25.7 g, 99%). ¹H NMR (CDCl₃, 300 MHz) δ 0.85-0.95 (6H, mult), 1.30-1.40 (8H, mult), 1.40-150 (4H, mult), 1.75-1.85 (4H, mult), 2.27 (3H, s), 3.94 (2H, t, J = 6.4 Hz), 4.01 (2H, t, J = 6.4 Hz), 6.79 (1H, s), 7.22 (1H, s), 10.41 (1H, s) ppm. ¹³C NMR (CDCl₃) δ 13.95 (CH₃), 17.21 (CH₃), 22.53 (CH₂), 22.55 (CH₂), 25.69 (CH₂), 25.72 (CH₂), 29.16 (CH₂), 31.47 (CH₂), 31.49 (CH₂), 68.40 (OCH₂), 69.10 (OCH₂), 108.19 (Ar CH), 115.58 (Ar CH), 122.96 (Ar quat), 136.71 (Ar quat), 151.32 (ArO quat), 156.12 (ArO quat), 189.31 (CHO) ppm. MS (EI): 320 (M⁺), 292, 236, 152 (base), 124, 91, 84 m/z. HRMS calcd for C₂₀H₃₂O₃: 320.2351 g/mol. Found: 320.2349 g/mol.



2,5-bis(hexyloxy)-4-methylbenzonitrile (12). Based on the methods of Olah,⁵ **11** (23.3 g, 73.6 mmol) and hydroxylamine hydrochloride (6.57 g, 94.5 mmol) were added to formic acid (100 mL) in a round-bottom flask and refluxed for 1 h. The dark mixture was poured into ice water (200 mL). The aqueous mixture was extracted with ether (3x50 mL). The combined organic layers were washed with brine (50 mL) and dried over MgSO₄. The solvent was removed *in vacuo*, and the residue was purified by column chromatography (silica gel, 99:1 hexanes:EtOAc)

to give the title compound as an orange liquid (17.1 g, 78%). ¹H NMR (CDCl₃, 300 MHz) δ 0.85-0.95 (6H, mult), 1.30-1.40 (8H, mult), 1.40-150 (4H, mult), 1.75-1.85 (4H, mult), 2.24 (3H, s), 3.87 (2H, t, J = 6.4 Hz), 3.98 (2H, t, J = 6.4 Hz), 6.75 (1H, s), 6.88 (1H, s) ppm. ¹³C NMR (CDCl₃) δ 13.87 (CH₃), 16.99 (CH₃), 22.43 (CH₂), 22.46 (CH₂), 25.43 (CH₂), 25.62 (CH₂), 28.94 (CH₂), 29.03 (CH₂), 31.38 (CH₂), 31.40 (CH₂), 68.63 (OCH₂), 69.44 (OCH₂), 98.53 (CN quat), 114.41 (Ar CH), 115.33 (Ar CH), 116.83 (Ar quat), 134.64 (Ar quat), 150.76 (ArO quat), 154.97 (ArO quat) ppm. . HRMS calcd for C₂₀H₃₂NO₂: 318.2433 g/mol. Found: 318.2435 g/mol.



2,5-bis(hexyloxy)-4-(dimethoxyphosphorylmethyl) benzonitrile (4 or **P-B-CN). 12** (13.8 g, 43.5 mmol) was dissolved in 1,2-dichloroethane (70 mL). NBS (3.90 g, 43.8 mmol), and benzoyl peroxide (0.540 g, 4.45 mmol) were added, and the mixture was refluxed until the orange color disappeared (2 h). NBS (3.90 g, 43.8 mmol), and benzoyl peroxide (0.540 g, 4.45 mmol) were added, and the mixture was refluxed for a second 2 h. After standing undisturbed overnight, the reaction mixture was filtered through a plug of silica and the solvent was removed *in vacuo*. The crude product was dissolved in PhMe (30 mL). Trimethyl phosphite (16.0 mL, 136 mmol) was added, and the mixture was refluxed overnight. The solvent was removed *in vacuo*, and the crude product was purified by column chromatography (silica gel, 1:1 hexanes:EtOAc) to give the title compound as a viscous orange liquid (11.7 g, 63% over 2 steps). ¹H NMR (CDCl₃, 300 MHz) δ 0.80-0.90 (6H, mult), 1.25-1.35 (8H, mult), 1.40-150 (4H, mult), 1.70-1.80 (4H, mult), 3.24 (2H, d, ²J_{H-P}=22.4 Hz), 3.66 (6H, d ³J_{H-P} = 11.2 Hz), 3.89 (2H, t, J = 6.4 Hz), 3.98 (2H, t,

Hz), 6.94 (1H, s), 6.96 (1H, d ${}^{4}J_{H-P} = 2.8$ Hz) ppm. ${}^{13}C$ NMR (CDCl₃) δ 13.83 (CH₃), 22.37 (CH₂), 22.41 (CH₂), 25.35 (CH₂), 25.50 (CH₂), 26.14 (d, ${}^{1}J_{C-P} = 138$ Hz, CH₂) 28.78 (CH₂), 28.97 (CH₂), 31.33 (CH₂), 31.34 (CH₂), 52.69 (d, ${}^{2}J_{C-P} = 7$ Hz, OCH₃) 69.08 (OCH₂), 69.45 (OCH₂), 100.24 (d, ${}^{6}J_{C-P} = 3$ Hz, CN quat), 115.36 (d, ${}^{4}J_{C-P} = 3$ Hz, Ar CH), 115.33 (d, ${}^{3}J_{C-P} = 5$ Hz, Ar CH), 116.31 (d, ${}^{5}J_{C-P} = 2$ Hz, Ar quat), 127.36 (d, ${}^{2}J_{C-P} = 9$ Hz, Ar quat), 150.06 (d, ${}^{3}J_{C-P} = 7$ Hz, ArO quat), 154.75 (d, ${}^{4}J_{C-P} = 3$ Hz, ArO quat) ppm. . HRMS calcd for C₂₂H₃₆NO₅P⁺Na: 448.2229 g/mol. Found: 448.2237 g/mol.

STEREOSELECTIVITY OF HWE REACTIONS²



Table S1. Stereoselectivity of HWE reactions

^a Estimated by ¹H NMR spectroscopy

In our initial investigations we encountered low stereoselectivity when using acetal-protected monomers – a perplexing result given the lack of discussion of stereoselectivity in reports of previous syntheses using the HWE reaction. Our model reactions were the HWE reaction between alkoxy-substituted bromobenzaldehyde **Br-B-CHO** (2) and either alkoxy-substituted phosphonate monomer 4 or 13, which we expected to be the most difficult HWE combinations

 $^{^{2}}$ A version of this table and the paragraph below it are also found in the paper but are repeated here with compoud numbers that correspond to the synthetic schemes and experimentals for specific compounds that are not included in the main text.

for steric reasons, to give the fully substituted dimers. The reaction with the acetal-protected monomer **13** (Table 1, entry 1) proceeded in quantitative yield and without loss of the bromine atom, as reported by Jørgensen and Krebs. This reaction, however, gave the dimer as a 2:1 mixture of *E* and *Z* isomers. As these isomers are difficult to separate by chromatography, we pursued further modifications. Addition of LiCl, which has been shown to increase *E*-selectivity in HWE reactions,^{6,7} increased the selectivity to 4:1 *E*:*Z* at the expense of conversion and yield (Table 1, entry 2). Nitrile monomer **4** (Table 1, entry 3) gave **Br-BB'-CN** in a 70% yield with higher *E*-selectivity (5:1). Addition of LiCl to this reaction increased both the yield to 100% and the *E*-selectivity to >9:1. Additionally, the CN-terminated oligomers were more easily purified by chromatography. The synthesis of compound **13** is outlined in Scheme **S1**, and the synthetic details follow.



Scheme S4. Synthesis of compound 13.



1,4-bis(hexyloxy)-2-(dimethoxyphosphorylmethyl)benzene (14). 9 (109.7 g, 375 mmol) was dissolved in CCl₄ (500 mL). NBS (33.7 g, 189 mmol) and AIBN (3.48 g, 37.8 mmol) were added, and the mixture was refluxed for 1.5 h. More NBS (33.7 g, 189 mmol) and AIBN (3.48 g, 37.8 mmol) were added, and the mixture was refluxed for another 1.5 h. The mixture was returned to rt and the succinimide was removed by filtration. The mixture was washed with H₂O (100 mL) and brine (100 mL) and dried over MgSO₄. The MgSO₄ was removed by filtration through a silica plug, which was washed with 3:1 hexanes:DCM. The combined filtrates were reduced in vacuo to give a mixture of regioisomers (3:2 benzyl:aryl bromide) (132 g, 95%). This mixture was dissolved in PhMe (250 mL). P(OCH₃)₃ (100 mL, 848 mmol) was added and the mixture was refluxed for 24 h. The volatiles were removed in vacuo. The crude product was purified by column chromatography (silica gel, 9:1 DCM:acetone) to give the title compound as a viscous yellow liquid (71.0 g, 47% over 2 steps). ¹H NMR (CDCl₃ 300 MHz) δ 0.80-0.90 (6H, mult), 1.15-1.45 (14H, mult), 1.60-1.75 (4H, mult), 3.18 (2H, d, ${}^{2}J_{H-P} = 21.6$ Hz), 3.61 (6H, d, ${}^{3}J_{\text{H-P}} = 11.7 \text{ Hz}$ 3.81 (2H, d, ${}^{3}J_{\text{H-H}} = 6.6 \text{ Hz}$), 3.86 (2H, d, ${}^{3}J_{\text{H-H}} = 6.9 \text{ Hz}$), 6.66 (1H, d, ${}^{3}J_{\text{H-H}} = 6.9 \text{ Hz}$) 8.7 Hz), 6.71 (1H, d, ${}^{3}J_{\text{H-H}} = 9.0$ Hz), 6.84 (1H, s) ppm.



2-(2,5-bis(hexvloxy)-4-(dimethoxyphosphorylmethyl)benzaldehyde (15). According to the methods of Bovicelli, et al.,⁸ 14 (65.0 g, 162 mmol) was dissolved in 1.5 L of dry DCM in a 3neck round-bottom flask under N₂ and cooled to 0 °C. AlCl₃ (43.3 g, 324 mmol) was added portionwise with vigorous stirring over15 min. The dark green mixture was stirred at 0 °C for another 15 min. A solution of CHCl₂OCH₃ (29 mL, 327 mmol) in dry DCM (300 mL) was added dropwise. The mixture was allowed to come to rt overnight with stirring. The dark red mixture was quenched by adding 1000 g of ice rapidly with vigorous stirring. The aqueous layer was extracted with DCM (4x 200 mL). The combined organic layer divided into two portions and washed with H₂O (300 mL) and brine (300 mL). The organic layers were dried over MgSO₄, and the solvent was removed *in vacuo*. The crude product was purified by column chromatography (silica DCM:acetone) 2,5-bis(hexyloxy)-4gel, 19:1 give to (dimethoxyphosphorylmethyl)benzaldehyde as 62.3 g of an orange liquid (89%). ¹H NMR (CDCl₃, 300 MHz) & 0.80-0.90 (6H, mult), 1.20-1.50 (14H, mult), 1.65-1.80 (4H, mult), 3.23 $(2H, d, {}^{2}J_{H-P} = 22.5 \text{ Hz}), 3.62 (6H, d, {}^{3}J_{H-P} = 10.8 \text{ Hz}), 3.91 (2H, t, {}^{3}J_{H-H} = 6.5 \text{ Hz}), 3.97 (2H, t, t)$ ${}^{3}J_{\text{H-H}} = 6.5 \text{ Hz}$, 6.97 (1H, d, ${}^{4}J_{\text{H-P}} = 2.7 \text{ Hz}$), 7.21 (1H, s), 10.36 (1H, s) ppm. ${}^{13}\text{C}$ NMR (CDCl₃, 75 MHz) δ 13.8 (CH₃), 22.3 (CH₂), 22.4 (CH₂), 25.5 (CH₂), 25.2 and 27.1 (d, ${}^{1}J_{C-P} = 142.5$ Hz PCH₂), 28.9 (CH₂), 29.0 (CH₂), 31.3 (CH₂), 52.5 (d, ${}^{2}J_{C-P} = 6.5$ Hz POCH₃), 68.6 (OCH₂), 68.9 (OCH₂), 108.9 (d, ${}^{4}J_{C-P} = 2.9$ Hz, Ar CH), 115.9 (d, ${}^{3}J_{C-P} = 5.6$ Hz, Ar CH), 123.7 (d, ${}^{5}J_{C-P} = 3.5$ Hz, Ar quat), 128.8 (d, ${}^{2}J_{C-P} = 9.5$ Hz, Ar quat), 150.4 (d, ${}^{3}J_{C-P} = 7.1$ Hz, ArO quat), 155.6 (d, ${}^{4}J_{C-P} = 7.1$ Hz, ArO quat), 155.6 (d, {}^{4}J_{C-P} = 7.1 Hz, ArO quat), 155.6 (d, {}^{4}J_{C-P} = 7.1 Hz, ArO quat), 155.6 (d, {}^{4}J_{C-P} = 7.1 $_{\rm P}$ = 3.7 Hz, ArO quat), 189.0 (d, $^{6}J_{\rm C-P}$ = 1.1 Hz, CHO) ppm.



2-(2,5-bis(hexyloxy)-4-(dimethoxyphosphorylmethyl)phenyl)-5,5-dimethyl-1,3-dioxane

(13). 15 (62.3 g, 144 mmol) was dissolved in PhMe (500 mL). Neopentylene glycol (22.5 g, 145 mmol) and TsOH (1.0 g, 7.13 mmol) were added and the mixture was refluxed for 24 h. The mixture was washed with H₂O (100 mL) and brine (100 mL) and dried over MgSO₄. The solvent was removed *in vacuo*. The crude product was purified by column chromatography (silica gel, 9:1 DCM:acetone) to give the title compound as an orange liquid (72.3 g, 97%). ¹H NMR (CDCl₃, 300 MHz) & 0.75 (3H, s, axial CH₃), 0.88-0.91 (6H, mult), 1.25-1.40 (11H, mult), 1.42-1.50 (4H, mult), 1.72-1.78 (4H, mult), 3.23 (2H, d, ${}^{2}J_{H-P} = 22.5$ Hz), 3.62 (6H, d, ${}^{3}J_{H-P} = 10.8$ Hz), 3.63 (2H, d, ${}^{2}J_{H-H} = 11.1$ Hz, axial CH), 3.73 (2H, d, ${}^{2}J_{H-H} = 11.1$ Hz, equatorial CH), 3.92 $(2H, t, {}^{3}J_{H-H} = 6.3 \text{ Hz}, \text{ OCH}_{2}), 3.97 (2H, t, {}^{3}J_{H-H} = 6.3 \text{ Hz}, \text{ OCH}_{2}), 6.89 (1H, d, {}^{4}J_{H-P} = 2.7 \text{ Hz}),$ 7.13 (1H, s) ppm. ¹³C NMR (CDCl₃, 75 MHz) & 13.9 (CH₃), 14.0 (CH₃), 21.8 (CH₃), 22.50 (CH₂), 22.54 (CH₂), 23.1 (CH₃), 25.6 (CH₂), 25.7 (CH₂), 25.1 (d, ${}^{1}J_{C-P} = 138.1$ Hz, ArCH₂P), 29.2 (CH₂), 29.3 (CH₂), 30.2 (quat), 31.5 (CH₂), 52.5 (d, ${}^{2}J_{C-P} = 6.6$ Hz, POCH₃), 68.8 (OCH₂), 69.4 (OCH₂), 77.8 (OCH₂), 97.0 (ArCHO₂), 110.3 (d, ${}^{4}J_{C-P} = 3.0$ Hz, Ar CH), 115.8 (d, ${}^{3}J_{C-P} =$ 5.1 Hz, Ar CH), 121.2 (d, ${}^{4}J_{C-P} = 9.5$ Hz, Ar quat), 126.5 (d, ${}^{5}J_{C-P} = 4.1.0$ Hz, Ar quat), 149.7 (d, ${}^{4}J_{C-P} = 3.7$ Hz, ArO quat), 150.8 (d, ${}^{3}J_{C-P} = 7.3$ Hz, ArO quat) ppm. MS (ESI): 537 (M+Na, base), 515, 497 m/z. HRMS calcd for C₂₇H₄₇O₇P+Na: 537.2957 g/mol. Found: 537.2954 g/mol.

SYNTHESIS OF OLIGOMERS

4-(4-bromostyryl)benzonitrile (Br-AA'-CN). This compound has been previously prepared by HWE reactions,⁹ but not from 4-bromobenzaldehyde and **P-A'-CN**. According to the general HWE procedure, 4-bromobenzaldehyde (1) (2.00 g, 10.8 mmol) , and **P-A'-CN (3)** (3.90 g, 16.2 mmol), and LiCl (1.40 g, 32.9 mmol) were dissolved in THF (100 mL) and cooled to 0 °C under N₂. KOtBu (3.60 g, 32.1 mmol) was added portionwise over 5 minutes, and the reaction was allowed to come to rt overnight with stirring. After workup, column chromatography (silica gel, 1:1 hexanes:DCM) gave the title compound as a white solid (2.60 g, 9.20 mmol, 85%)). ¹H NMR (CD₂Cl₂, 400 MHz) δ 7.11 (1H, d, *J* = 16.4 Hz, *trans* CH=CH), 7.18 (1H, d, *J* = 16.4 Hz, *trans* CH=CH), 7.42 (2H, d, *J* = 8.8 Hz, *p*-C₆H₄), 7.52 (2H, d, *J* = 8.8 Hz, *p*-C₆H₄), 7.59 (2H, d, *J* = 8.4 Hz, *p*-C₆H₄), 7.57 (2H, d, *J* = 8.4 Hz, *p*-C₆H₄), 119.41 (CN), 122.81 (ArBr quat), 127.45 (Ar CH), 127.99 (vinylene CH), 128.92 (Ar CH), 131.39 (vinylene CH), 132.46 (Ar CH), 133.06 (Ar CH), 135.97 (Ar quat), 141.96 (Ar quat) ppm. MS (EI) 285 (M+2), 283 (M⁺), 204, 203 (base), 177, 176, 151, 127, 103 m/z. HRMS calcd for C₁₅H₁₀NBr 282.9995 g/mol. Found: 282.9997 g/mol.



4-(4-bromostyryl)-2,5-bishexyloxybenzonitrile (Br-AB'-CN). According to the general HWE procedure, 4-bromobenzaldehvde (1) (611 mg, 3.30 mmol), P-B'-CN (4) (2.106 g, 4.95 mmol), and LiCl (321 mg, 7.57 mmol) were dissolved in THF (40 mL) and cooled to 0 °C under N₂. KO'Bu (850 mg, 7.57 mmol) was added portionwise over 5 minutes, and the reaction was allowed to come to rt overnight with stirring. After workup, column chromatography (silica gel, 9:1 hexanes: CHCl₃) gave the title compound as a pale yellow solid (1.414 g, 92%). ¹H NMR (CD₂Cl₂, 400 MHz) & 0.85-1.00 (6H, mult), 1.30-1.45 (8H, mult), 1.45-1.55 (4H, mult), 1.70-1.80 (4H, mult), 3.97 (2H, t, J = 6.4 Hz, OCH₂), 4.09 (2H, t, J = 6.4 Hz, OCH₂), 7.04 (1H, s), 7.158 (1H, s), 7.18 (1H, d, J = 17.2 Hz, trans CH=CH), 7.43 (2H, d, J = 8.0 Hz, p-C₆H₄), 7.44 (1H, d, J = 17.2 Hz, trans CH=CH), 7.51 (2H, d, J = 8.0 Hz, $p-C_6H_4$) ppm. ¹³C NMR (CD₂Cl₂, 100 MHz) § 14.36 (CH₃), 14.37 (CH₃), 23.15 (CH₂), 23.18 (CH₂), 26.11 (CH₂), 26.36 (CH₂), 29.61 (CH₂), 29.68 (CH₂), 32.07 (CH₂), 32.10 (CH₂), 70.11 (OCH₂), 70.24 (OCH₂), 101.18 (Ar quat), 110.76 (Ar CH), 117.04 (Ar CH), 117.15 (CN), 122.50 (ArBr quat), 123.60 (vinylene CH), 128.87 (Ar CH), 132.34 (vinvlene CH), 132.43 (Ar CH), 132.81 (Ar guat), 136.69 (Ar quat), 150.79 (ArO quat), 155.66 (ArO quat) ppm.



4-(4-bromo-2,5-bishexyloxystyryl)benzonitrile (Br-BA'-CN). According to the general HWE procedure, **Br-B-CHO (2)** (1.272 g, 3.30 mmol), **P-A'-CN (2)** (1.115 g, 4.95 mmol), and LiCl (321 mg, 7.57 mmol) were dissolved in THF (40 mL) and cooled to 0 °C under N₂. KO'Bu (850 mg, 7.57 mmol) was added portionwise over 5 minutes, and the reaction was allowed to come to rt overnight with stirring. After workup, column chromatography (silica gel, 4:1 hexanes:DCM) gave the title compound as a pale yellow solid (1.480 g, 96%). ¹H NMR (CD₂Cl₂, 400 MHz) δ 0.85-1.00 (6H, mult), 1.30-1.45 (8H, mult), 1.45-1.55 (4H, mult), 1.70-1.80 (4H, mult), 3.97 (2H, t, *J* = 6.4 Hz, OCH₂), 4.03 (2H, t, *J* = 6.4 Hz, OCH₂), 7.13 (1H, s), 7.13 (1H, s), 7.16 (1H, d, *J* = 16.4 Hz, *trans* CH=CH), 7.52 (1H, d, *J* = 16.4 Hz, *trans* CH=CH), 7.60 (2H, d, *J* = 8.4 Hz, *p*-C₆H₄) ppm. ¹³C NMR (CD₂Cl₂, 100 MHz) δ 14.36 (CH₃), 14.39 (CH₃), 23.18 (CH₂), 26.24 (CH₂), 26.39 (CH₂), 29.76 (CH₂), 29.81 (CH₂), 32.11 (CH₂), 70.18 (OCH₂), 70.72 (OCH₂), 111.04 (ArBr quat), 112.12 (Ar CH), 113.40 (Ar quat) 118.35 (Ar CH), 119.35 (CN), 125.93 (Ar quat), 127.15 (vinylene CH), 127.36 (Ar CH), 127.88 (vinylene CH), 133.03 (Ar CH), 142.75 (Ar quat), 150.34 (ArO quat), 151.95 (ArO quat) ppm.



4-(4-bromo-2,5-bishexyloxystyryl)-2,5-bishexyloxybenzonitrile (Br-BB'-CN). According to the general HWE procedure, Br-B-CHO (2) (1.272 g, 3.30 mmol), P-B'-CN (4) (2.106 g, 4.95

mmol), and LiCl (321 mg, 7.57 mmol) were dissolved in THF (40 mL) and cooled to 0 °C under N₂. KO^tBu (850 mg, 7.57 mmol) was added portionwise over 5 minutes, and the reaction was allowed to come to rt overnight with stirring. After workup, column chromatography (silica gel, 4:1 hexanes: DCM) gave the title compound as a bright yellow solid (2.240 g, 96%). ¹H NMR (CD₂Cl₂, 400 MHz) & 0.85-1.00 (12H, mult), 1.30-1.45 (16H, mult), 1.45-1.55 (8H, mult), 1.70-1.80 (8H, mult), 3.97 (4H, t, J = 6.4 Hz, OCH₂), 4.02 (2H, t, J = 6.4 Hz, OCH₂), 4.10 (2H, t, J =6.4 Hz, OCH₂), 7.04 (1H, s), 7.13 (1H, s), 7.15 (1H, s), 7.18 (1H, s), 7.45 (1H, d, J = 16.8 Hz, *trans* CH=CH), 7.51 (1H, d, J = 16.8 Hz, *trans* CH=CH) ppm. ¹³C NMR (CD₂Cl₂, 100 MHz) δ 14.38 (CH₃), 14.397 (CH₃), 23.16 (CH₂), 23.19 (CH₂), 23.21 (CH₂), 26.13 (CH₂), 26.26 (CH₂), 26.37 (CH₂), 29.64 (CH₂), 29.72 (CH₂), 29.79 (CH₂), 29.84 (CH₂), 32.09 (CH₂), 32.13 (CH₂), 70.04 (OCH₂), 70.11 (OCH₂), 70.18 (OCH₂), 70.69 (OCH₂), 100.82 (Ar quat), 110.73 (Ar CH), 112.26 (Ar CH), 113.06 (ArBr quat), 116.97 (Ar CH), 117.25 (CN), 118.28 (Ar CH), 123.56 (vinylene CH), 126.69 (Ar quat), 127.16 (vinylene CH), 133.66 (Ar quat), 150.34 (ArO quat), 150.73 (ArO quat), 151.89 (ArO quat), 155.70 (ArO quat) ppm. MS (EI): 685 (M+2, base), 683 (M⁺), 605, 349, 347, 267, 205, 85 m/z. HRMS calcd for C₃₉H₅₈NO₄Br: 683.3549 g/mol. Found: 683.3540 g/mol.



4-(4-bromostyryl)benzaldehyde (Br-AA'-CHO). This compound has been prepared before by Heck¹⁰ and HWE¹¹ reactions. Our methodology greatly increases yield. According to the general DIBAL-H procedure, **Br-AA'-CN** (448 mg, 1.80 mmol) was dissolved in DCM (10 mL) and cooled to 0 ^oC. DIBAL-H (1.0M in hexanes, 1.9 mL, 1.9 mmol) was added dropwise. After

workup, the solvent was removed *in vacuo* to give the title compound as a white solid (423 mg, 93%). ¹H NMR (CD₂Cl₂, 400 MHz) δ 7.17 (1H, d, *J* = 16.4 Hz, *trans* CH=CH), 7.24 (1H, d, *J* = 16.4 Hz, *trans* CH=CH), 7.45 (2H, d, *J* = 8.4 Hz, *p*-C₆H₄), 7.53 (2H, d, *J* = 8.4 Hz, *p*-C₆H₄), 7.68 (2H, d, *J* = 8.4 Hz, *p*-C₆H₄), 7.87 (2H, d, *J* = 8.4 Hz, *p*-C₆H₄), 9.99 (1H, s, CHO) ppm. ¹³C NMR (CD₂Cl₂, 100 MHz) δ 122.62 (ArBr quat), 127.52 (vinylene CH), 128.61 (Ar CH), 128.93 (vinylene CH), 130.63 (vinylene CH), 131.20 (Ar CH), 132.47 (Ar CH), 136.20 (Ar quat), 136.20 (Ar quat), 191.97 (CHO) ppm. MS (EI) 288 (M+2), 286 (M⁺), 178 (base), 152, 131, 107, 102, 89, 84, 76, 57 m/z. HRMS calcd for C₁₅H₁₁BrO: 285.9984 g/mol. Found: 285.9993 g/mol.



4-(4-bromostyryl)-2,5-bishexyloxybenzaldehyde (Br-AB'-CHO). According to the general DIBAL-H procedure, **Br-AB'-CN** (2.154 g, 4.446 mmol) was dissolved in DCM (25 mL) and cooled to 0 $^{\circ}$ C. DIBAL-H (1.0M in hexanes, 4.5 mL, 4.5 mmol) was added dropwise. After workup, column chromatography (silica gel, 3:2 hexanes:DCM) gave the title compound as a yellow oil that crystallized on standing (2.095 g, 95%). ¹H NMR (CD₂Cl₂, 400 MHz) δ 0.85-1.00 (6H, mult), 1.30-1.45 (8H, mult), 1.45-1.55 (4H, mult), 1.70-1.80 (4H, mult), 4.02 (2H, t, *J* = 6.4 Hz, OCH₂), 4.12 (2H, t, *J* = 6.4 Hz, OCH₂), 7.20 (1H, s), 7.30 (1H, s), 7.22 (1H, d, *J* = 16.4 Hz, *trans* CH=CH), 7.44 (2H, d, *J* = 8.4 Hz, *p*-C₆H₄), 7.49 (1H, d, *J* = 16.4 Hz, *trans* CH=CH), 7.51 (2H, d, *J* = 8.4 Hz, *p*-C₆H₄), 10.43 (1h, s, CHO) ppm. ¹³C NMR (CD₂Cl₂, 100 MHz) δ 14.37 (CH₃), 23.17 (CH₂), 23.19 (CH₂), 26.32 (CH₂), 26.42 (CH₂), 29.76 (CH₂), 29.78 (CH₂), 32.13 23

(CH₂), 32.14 (CH₂), 69.75 (OCH₂), 69.85 (OCH₂), 110.50 (Ar CH), 111.26 (Ar CH), 122.38 (ArBr quat), 124.14 (vinylene CH), 125.06 (Ar quat), 128.86 (Ar CH), 131.28 (vinylene CH), 132.40 (Ar CH), 134.13 (Ar quat), 136.89 (Ar quat), 151.33 (ArO quat), 156.68 (ArO quat), 189.25 (CHO) ppm. MS (EI): 488 (M+2), 486 (M⁺, base), 402, 374, 320, 318, 234, 206, 181, 165, 152, 119 m/z. HRMS calcd for C₂₇H₃₅O₃Br: 486.1770 g/mol. Found: 486.1763 g/mol.



4-(4-bromo-2,5-bishexyloxystyryl)benzaldehyde (Br-BA'-CHO). According to the general DIBAL-H procedure, **Br-BA'-CN** (2.560 g, 5.28 mmol) was dissolved in DCM (30 mL) and cooled to 0 $^{\circ}$ C. DIBAL-H (1.0M in hexanes, 5.3 mL, 5.3 mmol) was added dropwise. After workup, column chromatography (silica gel, 3:2 hexanes:DCM) gave the title compound as a yellow solid (2.420 g, 94%). ¹H NMR (CD₂Cl₂, 400 MHz) δ 0.85-1.00 (6H, mult), 1.30-1.45 (8H, mult), 1.45-1.55 (4H, mult), 1.70-1.80 (4H, mult), 3.98 (2H, t, *J* = 6.4 Hz, OCH₂), 4.04 (2H, t, *J* = 6.4 Hz, OCH₂), 7.13 (1H, s), 7.16 (1H, s), 7.21 (1H, d, *J* = 16.4 Hz, trans CH=CH), 7.57 (1H, d, *J* = 16.4 Hz, trans CH=CH), 7.68 (2H, d, *J* = 8.4 Hz, *p*-C₆H₄), 7.86 (2H, d, *J* = 8.4 Hz, *p*-C₆H₄), 9.98 (1H, s, CHO) ppm. ¹³C NMR (CD₂Cl₂, 100 MHz) δ 14.37 (CH₃), 14.39 (CH₃), 23.19 (CH₂), 26.25 (CH₂), 26.41 (CH₂), 29.79 (CH₂), 29.83 (CH₂), 32.13 (CH₂), 70.20 (OCH₂), 70.73 (OCH₂), 112.10 (Ar CH), 113.25 (ArBr quat), 118.36 (Ar CH), 126.19 (Ar quat), 126.93 (vinylene CH), 127.41 (Ar CH), 128.46 (vinylene CH), 130.62 (Ar CH), 135.96 (Ar quat), 144.27 (Ar quat), 150.35 (ArO quat), 151.95 (ArO quat), 191.95 (CHO) ppm.



4-(4-bromo-2,5-bishexyloxystyryl)-2,5-bishexyloxybenzaldehyde (Br-BB'-CHO). According to the general DIBAL-H procedure, Br-BB-CN (2.00 g, 2.92 mmol) was dissolved in DCM (20 mL) and cooled to 0 °C. DIBAL-H (1.0M in hexanes, 3.0 mL, 3.0 mmol) was added dropwise. After workup, column chromatography (silica gel, 4:1 hexanes:DCM) gave the title compound as a yellow solid (1.843 g, 92%). ¹H NMR (CD₂Cl₂, 400 MHz) δ 0.85-1.00 (12H, mult), 1.30-1.45 (16H, mult), 1.45-1.55 (8H, mult), 1.70-1.80 (8H, mult), 3.98 (2H, t, J = 6.4 Hz, OCH₂), 4.03 (2H, t, J = 6.4 Hz, OCH₂), 4.04 (2H, t, J = 6.4 Hz, OCH₂), 4.11 (2H, t, J = 6.4 Hz, OCH₂), 7.13 (1H, s), 7.17 (1H, s), 7.23 (1H, s), 7.30 (1H, s), 7.50 (1H, d, J = 16.8 Hz, trans CH=CH), 7.58 (1H, d, J = 16.8 Hz, trans CH=CH), 10.43 (1H, s, CHO) ppm. ¹³C NMR (CD₂Cl₂, 100 MHz) δ 14.40 (CH₃), 23.19 (CH₂), 23.24 (CH₂), 26.28 (CH₂), 26.35 (CH₂), 26.40 (CH₂), 29.42 (CH₂), 29.81 (CH₂), 29.83 (CH₂), 29.85 (CH₂), 32.14 (CH₂), 32.17 (CH₂), 32.18 (CH₂), 69.68 (OCH₂), 69.78 (OCH₂), 70.13 (OCH₂), 70.68 (OCH₂), 110.41 (Ar CH), 111.17 (Ar CH), 112.19 (Ar CH), 112.94 (ArBr quat), 118.29 (Ar CH), 124.05 (vinylene CH), 124.84 (Ar quat), 126.92 (Ar quat), 127.07 (vinylene CH), 135.02 (Ar quat), 150.35 (ArO quat), 151.28 (ArO quat), 151.89 (ArO quat), 156.75 (ArO quat), 189.25 (CHO) ppm. MS (ESI): 711 (M+Na+2, base), 709 (M+Na), 631, 527, 365 m/z. HRMS calcd for C₃₉H₅₉O₅Br+Na: 709.3444 g/mol. Found: 709.3455 g/mol.



4-(4-(4-bromostyryl)styryl)-2,5-bishexyloxybenzonitrile (Br-AAB'-CN). According to the general HWE procedure, Br-AA'-CHO (700 mg, 2.44 mmol), P-B'-CN (4) (1.557 g, 3.66 mmol), and LiCl (237 mg, 5.59 mmol) were dissolved in THF (30 mL) and cooled to 0 °C under N₂. KO^tBu (627 mg, 5.59 mmol) was added portionwise over 5 minutes, and the reaction was allowed to come to rt overnight with stirring. After workup, column chromatography (silica gel, 7:3 hexanes:DCM) gave the title compound as a yellow solid (1.166 g, 84%). ¹H NMR (CD₂Cl₂, 400 MHz) δ 0.93 (6H, t, J = 7.0 Hz), 1.30-1.40 (8H, mult), 1.50-1.60 (4H, mult), 1.86 (4H, pent, J = 7.3 Hz), 3.98 (2H, t, J = 6.4 Hz, OCH₂), 4.11 (2H, t, J = 6.4 Hz, OCH₂), 7.05 (1H, s), 7.09 (1H. d. J = 16.4 Hz, trans CH=CH), 7.14 (1H, d, J = 16.4 Hz, trans CH=CH), 7.19 (1H, s), 7.25 (1H, d, J = 16.4 Hz, trans CH=CH), 7.42 (2H, d, J = 8.8 Hz, $p-C_6H_4$), 7.48 (1H, d, J = 16.4 Hz, trans CH=CH), 7.50 (2H, d, J = 8.8 Hz, p-C₆H₄), 7.53 (2H, d, J = 8.8 Hz, p-C₆H₄), 7.56 (2H, d, J $= 8.8 \text{ Hz}, p-C_6H_4) \text{ ppm}.$ ¹³C NMR (CD₂Cl₂, 100 MHz) δ 14.38 (CH₃), 23.16 (CH₂), 23.18 (CH₂), 26.13 (CH₂), 26.39 (CH₂), 29.64 (CH₂), 29.73 (CH₂), 32.09 (CH₂), 32.13 (CH₂), 70.15 (OCH₂), 70.27 (OCH₂), 100.95 (ArCN quat), 110.66 (Ar CH), 117.07 (Ar CH), 117.23 (CN), 121.89 (ArBr quat), 122.83 (vinylene CH), 127.52 (Ar CH), 127.81 (Ar CH), 128.13 (vinylene CH), 128.60 (Ar CH), 129.35 (vinylene CH), 132.16 (vinylene CH), 132.36 (Ar CH), 133.22 (Ar quat), 136.86 (Ar quat), 137.28 (Ar quat), 137.59 (Ar quat), 150.80 (ArO quat), 155.72 (ArO quat) ppm. MS (ES): 587 (M+2), 585 (M⁺), 419, 420, 251, 228, 181, 169, 131, 119, 100, 69 (base), 55 m/z. HRMS calcd for C₃₅H₄₀NO₂Br: 585.2242 g/mol. Found: 585.2240 g/mol.



4-(4-(4-bromostyryl)-2,5-bishexyloxystyryl)-2,5-bishexyloxybenzonitrile (Br-ABB'-CN). According to the general HWE procedure, Br-AB'-CHO (850 mg, 1.74 mmol), P-B'-CN (4) (1.11 g, 2.61 mmol), and LiCl (170 mg, 4.01 mmol) were dissolved in THF (25 mL) and cooled to 0 °C under N₂. KO^tBu (450 mg, 4.01 mmol) was added portionwise over 5 minutes, and the reaction was allowed to come to rt overnight with stirring. After workup, column chromatography (silica gel, 4:1 hexanes:DCM) gave the title compound as a yellow solid (1.181 g, 86%). %). ¹H NMR (CD₂Cl₂, 400 MHz) δ 0.85-0.95 (12H, mult), 1.30-1.45 (16H, mult), 1.45-1.60 (8H, mult), 1.80-1.95 (8H, mult), 3.98 (2H, t, J = 6.4 Hz, OCH₂), 4.05 (2H, t, J = 6.4 Hz, OCH₂), 4.07 (2H, t, J = 6.4 Hz, OCH₂), 4.10 (2H, t, J = 6.4 Hz, OCH₂), 7.04 (1H, s), 7.13 (1H, d, J = 16.4 Hz, trans CH=CH), 7.14 (1H, s), 7.15 (1H, s), 7.20 (1H, s), 7.42 (2H, d, J = 8.4 Hz, p- C_6H_4), 7.46-7.51 (4H, mult) 7.59 (1H d, J = 16.8 Hz, trans CH=CH) ppm. ¹³C NMR (CD₂Cl₂, 100 MHz) § 14.37 (CH₃), 14.39 (CH₃), 23.16 (CH₂), 23.23 (CH₂), 23.25 (CH₂), 26.15 (CH₂), 26.39 (CH₂), 26.48 (CH₂), 26.54 (CH₂), 29.66 (CH₂), 29.75 (CH₂), 30.00 (CH₂), 32.10 (CH₂), 32.16 (CH₂), 32.16 (CH₂), 69.96 (OCH₂), 70.02 (OCH₂), 70.08 (OCH₂), 70.19 (OCH₂), 100.64 (ArCN guat), 110.59 (Ar CH), 110.91 (Ar CH), 111.31 (Ar CH), 117.07 (Ar CH), 117.32 (CN), 121.62 (ArBr quat), 122.99 (vinylene CH), 124.59 (vinylene CH), 127.22 (Ar quat), 127.50 (vinylene CH), 127.70 (Ar quat), 128.33 (vinylene CH), 128.56 (Ar CH), 132.31 (Ar CH) 133.97 (Ar quat), 137.50 (Ar quat), 150.74 (ArO quat), 151.66 (ArO quat), 151.94 (ArO quat), 155.72 (ArO quat) ppm. MS (ESI): 810 (M+Na+2, base), 808 (M+Na), 788, 786, 776, 685 (base)\m/z. HRMS calcd for C₄₇H₆₄NO₄Br+Na: 808.3916 g/mol. Found: 808.3965 g/mol.



4-(4-(4-bromostvrvl)-2.5-bishexvloxvstvrvl)benzonitrile (Br-ABA'-CN). According to the general HWE procedure, Br-AB'-CHO (850 mg, 1.74 mmol), P-A'-CN (3) (588 mg, 2.61 mmol), and LiCl (170 mg, 4.01 mmol) were dissolved in THF (25 mL) and cooled to 0 °C under N₂. KO^tBu (450 mg, 4.01 mmol) was added portionwise over 5 minutes, and the reaction was allowed to come to rt overnight with stirring. After workup, column chromatography (silica gel, 2:3 hexanes:DCM) gave the title compound as a vellow solid (950 mg, 92%). ¹H NMR (CD₂Cl₂, 400 MHz) δ 0.93 (6H, t, J = 7.0 Hz), 1.30-1.45 (8H, mult), 1.45-1.60 (4H, mult), 1.86 (4H, pent, J = 6.7 Hz), 4.06 (2H, t, J = 6.4 Hz, OCH₂), 4.07 (2H, t, J = 6.4 Hz, OCH₂), 7.13 (1H, d, J = 16.4Hz, trans CH=CH), 7.135 (1H, s), 7.138 (1H, s), 7.18 (1H, d, J = 16.4 Hz, trans CH=CH), 7.42 $(2H, d, J = 8.4 \text{ Hz}, p-C_6H_4), 7.48 (1H, d, J = 16.4 \text{ Hz}, trans CH=CH), 7.50 (2H, d, J = 8.4 \text{ Hz}, p-C_6H_4)$ C_6H_4), 7.61 (1H, d, J = 16.4 Hz, trans CH=CH), 7.61 (2H, d, J = 8.8 Hz, $p-C_6H_4$), 7.65 (2H, d, J $= 8.8 \text{ Hz}, p-C_6H_4) \text{ ppm}.$ ¹³C NMR (CD₂Cl₂, 100 MHz) δ 14.39 (CH₃), 23.23 (CH₂), 26.51 (CH₂), 29.98 (CH₂), 32.20 (CH₂), 70.02 (OCH₂), 70.06 (OCH₂), 110.83 (ArCN guat), 110.95 (Ar CH), 111.23 (Ar CH), 119.61 (CN), 121.66 (ArBr quat), 124.55 (vinylene CH), 126.44 (Ar quat), 127.57 (Ar CH), 127.39 (vinvlene CH), 127.57 (vinvlene CH), 127.98 (Ar guat) 128.48 (vinylene CH), 128.58 (Ar CH), 132.30 (vinylene CH), 133.02 (Ar CH), 137.45 (Ar quat), 143.03 (Ar guat), 151.64 (ArO guat), 152.02 (ArO guat) ppm. MS (ES): 587 (M+2), 585 (M⁺), 485, 483, 419, 417, 401, 317, 315, 290, 235, 206, 169, 152, 131, 116, 85, 69, 55 (base) m/z. HRMS calcd for C₃₅H₄₀NO₂Br: 585.2242 g/mol. Found: 585.2237 g/mol.



4-(4-(4-bromo-2,5-bishexyloxystyryl)benzonitrile (Br-BAA'-CN). According to the general HWE procedure, Br-BA'-CHO (1.10 g, 2.26 mmol), P-A'-CN (3) (761 mg, 3.38 mmol), and LiCl (220 mg, 4.01 mmol) were dissolved in THF (40 mL) and cooled to 0 °C under N₂. KO'Bu (583 mg, 5.19 mmol) was added portionwise over 5 minutes, and the reaction was allowed to come to rt overnight with stirring. After workup, column chromatography (silica gel, 2:3 hexanes:DCM) gave the title compound as a vellow solid (1.305 g, 99%). ¹H NMR (CD₂Cl₂, 400 MHz) δ 0.93 (6H, t, J = 6.4 Hz), 1.30-1.45 (8H, mult), 1.50-1.60 (4H, mult), 1.83 (2H, pent, J = 6.8 Hz), 1.85 (2H, pent, J = 6.8 Hz), 3.97 (2H, t, J = 6.4 Hz, OCH₂), 4.04 (2H, t, J = 6.4 Hz, OCH₂), 7.12 (1H, s), 7.14 (1H, d, J = 16.0 Hz, trans CH=CH), 7.16 (1H, s), 7.16 (1H, d, J = 16.4 Hz, trans CH=CH), 7.25 (1H, d, J = 16.0 Hz, trans CH=CH), 7.46 (1H, d, J = 16.4 Hz, trans CH=CH), 7.55 (4H, br s, *p*-C₆H₄), 7.61 (2H, d, *J* = 8.8 Hz, *p*-C₆H₄), 7.65 (2H, d, *J* = 8.8 Hz, *p*-C₆H₄) ppm. ¹³C NMR (CD₂Cl₂, 100 MHz) δ 14.39 (CH₃), 23.21 (CH₂), 26.26 (CH₂), 26.42 (CH₂), 29.84 (CH₂), 29.86 (CH₂), 32.14 (CH₂), 32.15 (CH₂), 70.22 (OCH₂), 70.74 (OCH₂), 110.10 (ArCN guat), 110.93 (Ar CH), 112.41 (ArBr guat), 118.35 (Ar CH), 119.52 (CN), 123.97 (vinylene CH), 126.87 (Ar guat), 127.06 (vinylene CH), 127.38 (Ar CH), 127.47 (Ar CH), 127.85 (Ar CH), 129.15 (vinylene CH), 132.34 (vinylene CH), 133.06 (Ar CH), 136.27 (Ar quat), 138.62 (Ar quat), 142.40 (Ar quat), 150.38 (ArO quat), 151.73 (ArO quat) ppm. MS (ESI): 610 (M+Na+2), 608 (M+Na), 527, 365 (base)\m/z. HRMS calcd for C₃₅H40NO₂Br+Na: 608.2140 g/mol. Found: 608.2094 g/mol.



4-(4-(4-bromo-2,5-bishexyloxystyryl)styryl)-2,5-bishexyloxystyrylbenzonitrile (Br-BAB'-CN). According to the general HWE procedure, Br-BA'-CHO (1.10 g, 2.26 mmol), P-B'-CN (4) (1.44 g, 3.38 mmol), and LiCl (220 mg, 4.01 mmol) were dissolved in THF (30 mL) and cooled to 0 °C under N2. KO'Bu (583 mg, 5.19 mmol) was added portionwise over 5 minutes, and the reaction was allowed to come to rt overnight with stirring. After workup, column chromatography (silica gel, 7:3 hexanes:DCM) gave the title compound as a yellow solid (1.687 g, 95%). ¹H NMR (CD₂Cl₂, 400 MHz) δ 0.85-0.95 (12H, mult), 1.30-1.45 (16H, mult), 1.45-1.60 (8H, mult), 1.80-1.95 (8H, mult), 3.97 (2H, t, J = 6.4 Hz, OCH₂), 3.98 (2H, t, J = 6.4 Hz, OCH₂), 4.04 (2H, t, J = 6.4 Hz, OCH₂), 4.11 (2H, t, J = 6.4 Hz, OCH₂), 7.04 (1H, s), 7.12 (1H, s), 7.16 (1H, d, J = 16.4 Hz, trans CH=CH), 7.16(1H, s), 7.19 (1H, s), 7.25 (1H, d, J = 16.4 Hz, trans CH=CH), 7.46 (1H, d, J = 16.4 Hz, trans CH=CH), 7.48 (1H, d, J = 16.4 Hz, trans CH=CH), 7.55 (4H, br s, *p*-C₆H₄) ppm. ¹³C NMR (CD₂Cl₂, 100 MHz) δ 14.39 (CH₃), 23.18 (CH₂), 23.21 (CH₂), 26.14 (CH₂), 26.27 (CH₂), 26.41 (CH₂), 26.44 (CH₂), 29.66 (CH₂), 29.74 (CH₂), 29.86 (CH₂), 29.87 (CH₂), 32.11 (CH₂), 32.15 (CH₂), 32.17 (CH₂), 70.15 (OCH₂), 70.23 (OCH₂), 70.26 (OCH₂), 70.75 (OCH₂), 100.88 (ArCN quat), 110.60 (Ar CH), 111.89 (Ar CH), 112.35 (ArBr quat), 117.05 (Ar CH), 117.25 (CN), 118.35 (Ar CH), 122.60 (vinylene CH), 123.77 (vinylene CH), 126.92 (Ar quat), 127.45 (Ar CH), 127.79 (Ar CH), 129.21 (vinylene CH), 133.27 (vinylene CH) 133.27 (Ar quat), 136.99 (Ar quat), 138.36 (Ar quat), 150.38 (ArO quat), 150.78 (ArO quat), 151.72 (ArO quat), 155.73 (ArO quat) ppm. MS (ESI): 810 (M+Na+2), 808

(M+Na), 788, 786, 711, 709, 691, 527 (base)\m/z. HRMS calcd for C₄₇H₆₄NO₄Br+Na: 808.3916 g/mol. Found: 808.4011 g/mol.



4-(4-(4-bromo-2,5-bishexyloxystyryl)-2,5-bishexyloxystyrylstyryl)benzonitrile (Br-BBA'-CN). According to the general HWE procedure, Br-BB'-CHO (1.64 g, 2.39 mmol), P-A'-CN (3) (807 mg, 3.58 mmol),-were dissolved in THF (30 mL) and cooled to 0 °C under N₂. KO'Bu (618 mg, 5.50 mmol) was added portionwise over 5 minutes, and the reaction was allowed to come to rt overnight with stirring. After workup, column chromatography (silica gel, 1:1 hexanes:DCM) gave the title compound as a yellow solid (1.610 g, 86%). ¹H NMR (CD₂Cl₂, 400 MHz) & 0.85-0.95 (12H, mult), 1.30-1.45 (16H, mult), 1.45-1.60 (8H, mult), 1.80-1.95 (8H, mult), 3.98 (2H, t, J = 6.4 Hz, OCH₂), 4.04 (2H, t, J = 6.4 Hz, OCH₂), 4.06 (2H, t, J = 6.4 Hz, OCH₂), 4.07 (2H, t, J = 6.4 Hz, OCH₂), 7.11 (1H, s), 7.14 (1H, s), 7.17 (1H, s), 7.18 (1H, d, J = 16.4 Hz, trans CH=CH), 7.18 (1H, s), 7.45 (1H, d, J = 16.8 Hz, trans CH=CH), 7.50 (1H, d, J = 16.8 Hz, trans CH=CH), 7.62 (1H, d, J = 16.4 Hz, trans CH=CH), 7.62 (2H, d, J = 8.8 Hz, p- $C_{6}H_{4}$, 7.65 (2H, d, J = 8.8 Hz, $p-C_{6}H_{4}$) ppm. ¹³C NMR (CD₂Cl₂, 100 MHz) δ 14.40 (CH₃), 14.42 (CH₃), 14.43 (CH₃), 23.20 (CH₂), 23.24 (CH₂), 23.26 (CH₂), 26.29 (CH₂), 26.42 (CH₂), 26.50 (CH₂), 26.54 (CH₂), 29.88 (CH₂), 30.00 (CH₂), 30.02 (CH₂), 32.15 (CH₂), 32.19 (CH₂), 32.21 (CH₂), 32.24 (CH₂), 69.97 (OCH₂), 70.00 (OCH₂), 70.15 (OCH₂), 70.69 (OCH₂), 110.78 (Ar CH), 110.95 (Ar CH), 111.17 (ArCN guat), 111.95 (Ar CH), 112.13 (ArBr guat), 118.28 (Ar CH), 119.62 (CN), 124.15 (vinylene CH), 124.42 (vinylene CH), 126.14 (Ar guat), 127.21

(vinylene CH), 127.30 (Ar CH), 127.55 (Ar quat), 127.64 (vinylene CH), 128.81 (Ar quat), 133.03 (Ar CH), 143.10 (Ar quat), 150.37 (ArO quat), 151.58 (ArO quat), 151.68 (ArO quat), 152.05 (ArO quat) ppm. MS (ESI): 810 (M+Na+2), 808 (M+Na), 788, 786, 711, 709, 691, 527 (base)\m/z. HRMS calcd for $C_{47}H_{64}NO_4Br$ +Na: 808.3916 g/mol. Found: 808.4011 g/mol. MS (ESI): 810 (M+Na+2), 808 (M+Na), 786, 776, 707, 527, 365 (base)\m/z. HRMS calcd for $C_{47}H_{64}NO_4Br$ +Na: 808.3916 g/mol. Found: 808.4011 g/mol. MS (ESI): 810 (M+Na+2), 808 (M+Na), 786, 776, 707, 527, 365 (base)\m/z. HRMS calcd for $C_{47}H_{64}NO_4Br$ +Na: 808.3916 g/mol. Found: 808.3916 g/mol.



4-(4-(4-bromostyryl)styryl)-2,5-bishexyloxybenzaldehyde (Br-AAB'-CHO). According to the general DIBAL-H procedure, **Br-AAB'-CN** (375 mg, 0.635 mmol) was dissolved in DCM (5 mL) and cooled to 0 $^{\text{O}}$ C. DIBAL-H (1.0M in hexanes, 0.75 mL, 0.75 mmol) was added dropwise. After workup, column chromatography (silica gel, 7:3 hexanes:DCM) gave the title compound as a yellow solid (308 mg, 82%). ¹H NMR (CD₂Cl₂, 400 MHz) δ 0.93 (6H, t, *J* = 7.0 Hz), 1.30-1.40 (8H, mult), 1.50-1.60 (4H, mult), 1.86 (4H, pent, *J* = 7.1 Hz), 4.04 (2H, t, *J* = 6.4 Hz, OCH₂), 4.12 (2H, t, *J* = 6.4 Hz, OCH₂), 7.09 (1H, d, *J* = 16.4 Hz, *trans* CH=CH), 7.14 (1H, d, *J* = 16.4 Hz, *trans* CH=CH), 7.22 (1H, s), 7.28 (1H, d, *J* = 16.4 Hz, *trans* CH=CH), 7.30 (1H, s), 7.41 (2H, d, *J* = 8.8 Hz, *p*-C₆H₄), 7.50 (2H, d, *J* = 8.8 Hz, *p*-C₆H₄), 7.53 (1H, d, *J* = 16.4 Hz, *trans* CH=CH), 7.54 (2H, d, *J* = 8.8 Hz, *p*-C₆H₄), 7.57 (2H, d, *J* = 8.4 Hz, *p*-C₆H₄), 10.44 (1H, s, CHO) ppm. ¹³C NMR (CD₂Cl₂, 100 MHz) δ 14.39 (CH₃), 23.16 (CH₂), 23.18 (CH₂), 23.21 (CH₂), 26.33 (CH₂), 26.44 (CH₂), 29.79 (CH₂), 32.13 (CH₂), 32.17 (CH₂), 69.76 (OCH₂), 69.84 (OCH₂), 110.47 (Ar CH), 111.07 (Ar CH), 121.85 (ArBr quat), 123.35 (vinylene CH), 124.89

(Ar quat), 127.51 (Ar CH), 127.79 (Ar CH), 128.03 (vinylene CH), 128.58 (Ar CH), 129.37 (vinylene CH), 132.11 (vinylene CH), 132.34 (Ar CH), 133.53 (Ar quat), 136.87 (Ar quat), 137.47 (Ar quat), 151.32 (ArO quat), 156.73 (ArO quat) 189.24 (CHO) ppm. MS (ES): 590 (M+2), 588 (M⁺), 420, 288, 286, 178 (base), 152, 131, 102, 90, 77, 69, 55 m/z. HRMS calcd for $C_{35}H_{41}O_{3}Br$: 588.2239 g/mol. Found: 588.2239 g/mol.



4-(4-(4-bromostyryl)-2,5-bishexyloxystyryl)-2,5-bishexyloxybenzaldehyde (Br-ABB'-CHO). According to the general DIBAL-H procedure, **Br-ABB'-CN** (500 mg, 0.635 mmol) was dissolved in DCM (5 mL) and cooled to 0 $^{\text{O}}$ C. DIBAL-H (1.0M in hexanes, 0.75 mL, 0.75 mmol) was added dropwise. After workup, column chromatography (silica gel, 7:3 hexanes:DCM) gave the title compound as a yellow solid (409 mg, 82%). ¹H NMR (CD₂Cl₂, 400 MHz) & 0.85-0.95 (12H, mult), 1.30-1.45 (16H, mult), 1.45-1.60 (8H, mult), 1.80-1.95 (8H, mult), 4.05 (2H, t, J = 6.4 Hz, OCH₂), 4.06 (2H, t, J = 6.4 Hz, OCH₂), 4.07 (2H, t, J = 6.4 Hz, OCH₂), 7.04 (1H, s), 4.14 (2H, t, J = 6.4 Hz, OCH₂), 7.13 (1H, d, J = 16.4 Hz, *trans* CH=CH), 7.15 (1H, s), 7.17 (1H, s), 7.25 (1H, s), 7.30 (1H, s), 7.43 (2H, d, J = 8.4 Hz, p-C₆H₄), 7.50 (1H d, J = 16.4 Hz, *trans* CH=CH), 7.53 (1H d, J = 16.8 Hz, *trans* CH=CH), 7.63 (1H d, J = 16.8 Hz, *trans* CH=CH), 10.43 (1H, s, CHO) ppm. ¹³C NMR (CD₂Cl₂, 100 MHz) & 14.38 (CH₃), 14.41 (CH₃), 23.18 (CH₂), 23.24 (CH₂), 23.26 (CH₂), 26.35 (CH₂), 26.44 (CH₂), 26.50 (CH₂), 26.53 (CH₂), 29.81 (CH₂), 30.00 (CH₂), 32.14 (CH₂), 32.19 (CH₂), 32.20 (CH₂), 32.23 (CH₂), 69.70 (OCH₂), 69.78 (OCH₂), 69.96 (OCH₂), 69.99 (OCH₂), 110.40 (Ar CH), 110.90 (Ar CH), 110.99 (Ar CH), 111.22 (Ar CH), 121.59 (ArBr quat), 123.49 (vinylene CH), 124.61 (vinylene CH), 124.72 (Ar quat), 127.43 (Ar quat), 127.43 (vinylene CH), 127.57 (Ar quat), 128.24 (vinylene CH), 128.55 (Ar CH), 132.30 (Ar CH) 135.31 (Ar quat), 137.51 (Ar quat), 151.27 (ArO quat), 151.67 (ArO quat), 151.92 (ArO quat), 156.79 (ArO quat), 189.25 (CHO) ppm.



4-(4-(4-bromostyryl)-2,5-bishexyloxystyryl)benzaldehyde (Br-ABA'-CHO). According to the general DIBAL-H procedure, **Br-ABA'-CN** (375 mg, 0.635 mmol) was dissolved in DCM (5 mL) and cooled to 0 ^oC. DIBAL-H (1.0M in hexanes, 0.75 mL, 0.75 mmol) was added dropwise. After workup, column chromatography (silica gel, 2:3 hexanes:DCM) gave the title compound as a yellow solid (302 mg, 81%). ¹H NMR (CD₂Cl₂, 400 MHz) δ 0.94 (6H, t, J = 6.8 Hz), 1.30-1.45 (8H, mult), 1.45-1.60 (4H, mult), 1.80-1.95 (4H, mult), 4.06 (2H, t, J = 6.4 Hz, OCH₂), 4.07 (2H, t, J = 6.4 Hz, OCH₂), 7.13 (1H, d, J = 16.4 Hz, *trans* CH=CH), 7.14 (1H, s), 7.15 (1H, s), 7.23 (1H, d, J = 16.8 Hz, *trans* CH=CH), 7.42 (2H, d, J = 8.4 Hz, *p*-C₆H₄), 7.49 (1H, d, J = 16.4 Hz, *trans* CH=CH), 7.50 (2H, d, J = 8.4 Hz, *p*-C₆H₄), 7.60 (1H, d, J = 16.8 Hz, *trans* CH=CH), 7.69 (2H, d, J = 8.4 Hz, *p*-C₆H₄), 7.86 (2H, d, J = 8.4 Hz, *p*-C₆H₄), 9.98 (CHO) ppm. ¹³C NMR (CD₂Cl₂, 100 MHz) δ 14.41 (CH₃), 23.24 (CH₂), 26.53 (CH₂), 30.00 (CH₂), 32.21 (CH₂), 70.04 (OCH₂), 110.93 (Ar CH), 111.16 (Ar CH), 121.63 (ArBr quat), 124.57 (vinylene CH), 126.69 (Ar quat), 127.36 (Ar CH), 130.62 (Ar CH), 132.30 (Ar CH),

135.83 (Ar quat), 137.47 (Ar quat) 144.56 (Ar quat), 151.65 (ArO quat), 152.00 (ArO quat), 191.94 (CHO) ppm. MS (ES): 590 (M+2), 588 (M⁺), 504, 476, 420, 422, 340, 265, 149, 131, 127, 91, 85, 69 (base) m/z. HRMS calcd for C₃₅H₄₁O₃Br: 588.2239 g/mol. Found: 588.2231 g/mol.



4-(4-(4-bromo-2,5-bishexyloxystyryl)styryl)benzaldehyde (Br-BAA'-CHO). According to the general DIBAL-H procedure, Br-BAA'-CN (375 mg, 0.635 mmol) was dissolved in DCM (5 mL) and cooled to 0 °C. DIBAL-H (1.0M in hexanes, 0.75 mL, 0.75 mmol) was added dropwise. After workup, column chromatography (silica gel, 7:3 hexanes:DCM) gave the title compound as a yellow solid (348 mg, 93%). ¹H NMR (CD₂Cl₂, 400 MHz) δ 0.95 (6H, t, J = 6.0 Hz), 1.30-1.45 (8H, mult), 1.50-1.60 (4H, mult), 1.83 (2H, pent, J = 6.8 Hz), 1.85 (2H, pent, J =6.8 Hz), 3.97 (2H, t, J = 6.4 Hz, OCH₂), 4.04 (2H, t, J = 6.4 Hz, OCH₂), 7.12 (1H, s), 7.16 (1H, d, J = 16.8 Hz, trans CH=CH), 7.16 (1H, s), 7.19 (1H, d, J = 16.4 Hz, trans CH=CH), 7.29 (1H, d, J = 16.4 Hz, trans CH=CH), 7.46 (1H, d, J = 16.8 Hz, trans CH=CH), 7.56 (4H, br s, p-C₆H₄), 7.68 (2H, d, J = 8.4 Hz, $p-C_6H_4$), 7.87 (2H, d, J = 8.4 Hz, $p-C_6H_4$), 9.98 (1H, s, CHO) ppm. ¹³C NMR (CD₂Cl₂, 100 MHz) δ 14.40 (CH₃), 23.20 (CH₂), 23.22 (CH₂), 26.26 (CH₂), 26.42 (CH₂), 29.84 (CH₂), 29.86 (CH₂), 32.14 (CH₂), 32.15 (CH₂), 70.20 (OCH₂), 70.72 (OCH₂), 111.88 (Ar CH), 112.35 (ArBr quat), 118.32 (Ar CH), 123.87 (vinylene CH), 126.87 (Ar quat), 127.41 (Ar CH), 127.46 (Ar CH), 127.63 (vinylene CH), 127.83 (Ar CH), 129.18 (vinylene CH), 130.63 (Ar CH), 132.34 (vinylene CH), 135.98 (Ar guat), 136.49 (Ar guat), 138.49 (Ar guat), 143.89 (Ar

quat), 150.35 (ArO quat), 151.70 (ArO quat), 191.92 (CHO) ppm. MS (ES): 590 (M+2), 588 (M⁺), 422, 420, 221, 181, 131, 119, 100, 85, 69 (base) m/z. HRMS calcd for C₃₅H₄₁O₃Br: 588.2239 g/mol. Found: 588.2230 g/mol.



4-(4-(4-bromo-2,5-bishexvloxvstvrvl)stvrvl)-2,5-bishexvloxvstvrvlbenzaldehvde (Br-BAB'-CHO). According to the general DIBAL-H procedure, Br-BAB'-CN (500 mg, 0.635 mmol) was dissolved in DCM (5 mL) and cooled to 0 °C. DIBAL-H (1.0M in hexanes, 0.75 mL, 0.75 mmol) was added dropwise. After workup, column chromatography (silica gel, 2:3 hexanes:DCM) gave the title compound as a vellow solid (426 mg, 85%). ¹H NMR (CD₂Cl₂, 400 MHz) & 0.85-0.95 (12H, mult), 1.30-1.45 (16H, mult), 1.45-1.60 (8H, mult), 1.80-1.95 (8H, mult), 3.97 (2H, t, J = 6.4 Hz, OCH₂), 4.04 (4H, t, J = 6.4 Hz, OCH₂), 4.12 (2H, t, J = 6.4 Hz, OCH₂), 7.12 (1H, s), 7.16 (1H, s), 7.17 (1H, d, J = 16.4 Hz, trans CH=CH), 7.23 (1H, s), 7.29 (1H, d, J = 16.4 Hz, trans CH=CH), 7.31 (1H, s), 7.46 (1H, d, J = 16.4 Hz, trans CH=CH), 7.53 (1H, d, J = 16.4 Hz, trans CH=CH), 7.56 (4H, br s, p-C₆H₄), 10.44 ppm (1H, s, CHO) ppm. ¹³C NMR (CD₂Cl₂, 100 MHz) δ 14.41 (CH₃), 23.23 (CH₂), 26.29 (CH₂), 26.36 (CH₂), 26.45 (CH₂), 26.47 (CH₂), 29.83 (CH₂), 29.87 (CH₂), 32.16 (CH₂), 32.18 (CH₂), 32.20 (CH₂), 69.78 (OCH₂), 69.85 (OCH₂), 70.22 (OCH₂), 70.73 (OCH₂), 110.49 (Ar CH), 111.03 (Ar CH), 111.97 (Ar CH), 112.32 (ArBr quat), 118.35 (Ar CH), 123.16 (vinylene CH), 123.70 (vinylene CH), 124.88 (Ar quat) 126.95 (Ar quat), 127.44 (Ar CH), 127.78 (Ar CH), 129.25 (vinvlene CH), 133.20 (vinylene CH) 134.61 (Ar guat), 137.21 (Ar guat), 138.26 (Ar guat), 150.38 (ArO guat), 151.33
(ArO quat), 151.71 (ArO quat), 156.76 (ArO quat), 189.22 (CHO) ppm. MS (ESI): 813 (M+Na+2), 811 (M+Na), 527, 365 (base)\m/z. HRMS calcd for C₄₇H₆₄NO₄Br+Na: 811.3913 g/mol. Found: 811.3898 g/mol.



4-(4-(4-bromo-2,5-bishexvloxvstvrvl)-2,5-bishexvloxvstvrvlstvrvl)benzaldehvde (Br-BBA'-CHO). According to the general DIBAL-H procedure, Br-BBA'-CN (500 mg, 0.635 mmol) was dissolved in DCM (5 mL) and cooled to 0 °C. DIBAL-H (1.0M in hexanes, 0.75 mL, 0.75 mmol) was added dropwise. After workup, column chromatography (silica gel, 7:3 hexanes:DCM) gave the title compound as a vellow solid (490 mg, 98%). ¹H NMR (CD₂Cl₂, 400 MHz) & 0.85-0.95 (12H, mult), 1.30-1.45 (16H, mult), 1.45-1.60 (8H, mult), 1.80-1.95 (8H, mult), 3.98 (2H, t, J = 6.4 Hz, OCH₂), 4.04 (2H, t, J = 6.4 Hz, OCH₂), 4.07 (2H, t, J = 6.4 Hz, OCH₂), 4.08 (2H, t, J = 6.4 Hz, OCH₂), 7.11 (1H, s), 7.16 (1H, s), 7.17 (1H, s), 7.18 (1H, s), 7.24 (1H, d, J = 16.4 Hz, trans CH=CH), 7.45 (1H, d, J = 16.8 Hz, trans CH=CH), 7.50 (1H, d, J = 16.8 Hz, trans CH=CH), 7.67 (1H, d, J = 16.4 Hz, trans CH=CH), 7.69 (2H, d, J = 8.0 Hz, p- C_6H_4), 7.86 (2H, d, J = 8.0 Hz, $p-C_6H_4$), 9.98 (1H, s, CHO) ppm. ¹³C NMR (CD₂Cl₂, 100 MHz) δ 14.42 (CH₃), 23.20 (CH₂), 23.24 (CH₂), 23.26 (CH₂), 26.28 (CH₂), 26.41 (CH₂), 26.50 (CH₂), 26.55 (CH₂), 29.87 (CH₂), 30.02 (CH₂), 32.15 (CH₂), 32.18 (CH₂), 32.22 (CH₂), 32.23 (CH₂), 70.00 (OCH₂), 70.16 (OCH₂), 70.69 (OCH₂), 110.97 (Ar CH), 111.15 (Ar CH), 111.94 (Ar CH), 112.10 (ArBr quat), 118.29 (Ar CH), 124.07 (vinylene CH), 124.45 (vinylene CH), 126.41 (Ar guat), 127.43 (vinylene CH), 127.34 (Ar CH), 127.59 (Ar guat), 127.81 (vinylene CH), 128.68 (Ar quat), 130.63 (Ar CH), 144.63 (Ar quat), 150.37 (ArO quat), 151.59 (ArO quat), 151.67 (ArO quat), 152.05 (ArO quat), 191.94 (CHO) ppm. MS (ESI): 813 (M+Na+2), 811 (M+Na), 776, 711, 709, 691, 527, 365 (base) m/z. HRMS calcd for C₄₇H₆₅O₅Br+Na: 811.3913 g/mol. Found: 811.3935 g/mol.



4-(4-(4-(4-bromostvryl)styryl)-2,5-bishexyloxystyryl)-2,5-bishexyloxybenzonitrile (Br-AABB'-CN). According to the general HWE procedure, Br-AAB'-CHO (200 mg, 0.341 mmol), **P-B'-CN** (4) (220 mg, 0.517 mmol), and LiCl (34.0 mg, 0.802 mmol) were dissolved in THF (5 mL) and cooled to 0 °C under N₂. KO^tBu (88.0 mg, 0.784 mmol) was added portionwise over 5 minutes, and the reaction was allowed to come to rt overnight with stirring. After workup, column chromatography (silica gel, 13:7 hexanes:DCM) gave the title compound as an orange solid (293 mg, 97%). ¹H NMR (CD₂Cl₂, 400 MHz) δ 0.85-1.00 (12H, mult), 1.30-1.45 (16H, mult), 1.45-1.60 (8H, mult), 1.80-1.95 (8H, mult), 3.99 (2H, t, J = 6.4 Hz, OCH₂), 4.06 (2H, t, J = 6.4 Hz, OCH₂), 4.08 (2H, t, J = 6.4 Hz, OCH₂), 4.11 (2H, t, J = 6.4 Hz, OCH₂), 7.04 (1H, s), 7.08 (1H, d, J = 16.4 Hz, trans CH=CH), 7.14 (1H, d, J = 16.4 Hz, trans CH=CH), 7.16 (1H, s), 7.17 (1H, s), 7.20 (1H, d, J = 16.4 Hz, trans CH=CH), 7.21 (1H, s) 7.42 (2H, d, J = 8.4 Hz, p- C_6H_4), 7.47-7.57 (8H, mult), 7.60 (1H, d, J = 16.4 Hz, trans CH=CH) ppm. ¹³C NMR (CD₂Cl₂, 100 MHz) & 14.38 (CH₃), 14.42 (CH₃), 23.17 (CH₂), 23.23 (CH₂), 23.25 (CH₂), 23.27 (CH₂), 26.15 (CH₂), 26.39 (CH₂), 26.50 (CH₂), 26.55 (CH₂), 29.66 (CH₂), 29.76 (CH₂), 30.01 (CH₂), 30.03 (CH₂), 32.10 (CH₂), 32.17 (CH₂), 32.23 (CH₂), 69.92 (OCH₂), 70.01 (OCH₂), 70.05

(OCH₂), 70.16 (OCH₂), 100.56 (ArCN, quat), 110.51 (Ar CH), 110.74 (Ar CH), 111.28 (Ar CH), 116.95 (Ar CH), 117.34 (CN), 121.73 (ArBr quat), 122.82 (vinylene CH), 123.84 (vinylene CH), 126.98 (Ar quat), 127.43 (Ar CH), 128.43 (Ar CH), 128.52 (vinylene CH), 127.63 (vinylene CH), 128.05 (Ar quat), 128.05 (Ar CH), 128.55 (vinylene CH), 129.51 (vinylene CH), 132.32 (Ar CH), 133.98 (Ar quat), 136.83 (Ar quat), 136.97 (Ar quat), 138.11 (Ar quat), 150.72 (ArO quat), 151.63 (ArO quat), 151.96 (ArO quat), 155.72 (ArO quat) ppm. HRMS calc. for $C_{55}H_{71}NO_4Br$: 888.4566 g/mol. Found: 888.4554 g/mol.



4-(4-(4-(4-(4-(4-bromostyryl)-2,5-bishexyloxystyryl)-2,5-bishexyloxystyryl)benzonitrile (Br-ABBA'-CN). According to the general HWE procedure, Br-ABB'-CHO (300 mg, 0.380 mmol), P-A'-CN (3) (130 mg, 0.577 mmol), and LiCl (37.0 mg, 0.873 mmol) were dissolved in THF (40 mL) and cooled to 0 °C under N₂. KO'Bu (98.0 mg, 0.873 mmol) was added portionwise over 5 minutes, and the reaction was allowed to come to rt overnight with stirring. After workup, column chromatography (silica gel, 4:1 hexanes:DCM) gave the title compound as an orange solid (300 mg, 89%). ¹H NMR (CD₂Cl₂, 400 MHz) δ 0.85-1.00 (12H, mult), 1.30-1.45 (16H, mult), 1.45-1.60 (8H, mult), 1.80-1.95 (8H, mult), 4.05-4.10 (8H, mult), 7.11-7.19 (6H, mult), 7.42 (2H, d, J = 8.4 Hz, p-C₆H₄), 7.48-7.52 (5H, mult), 7.61-7.66 (5H, mult) ppm. ¹³C NMR (CD₂Cl₂, 100 MHz) δ 13.83 (CH₃), 13.87 (CH₃), 22.67 (CH₂), 22.70 (CH₂), 25.95 (CH₂), 25.98 (CH₂), 29.44 (CH₂), 29.47 (CH₂), 31.65 (CH₂), 31.68 (CH₂), 69.38 (OCH₂), 69.42 (OCH₂), 69.46 (OCH₂), 110.18 (ArCN, quat), 110.21 (Ar CH), 110.32 (Ar CH), 110.36 (Ar CH), 110.35 (Ar

CH), 119.07 (CN), 120.91 (ArBr quat), 123.33 (vinylene CH), 123.93 (vinylene CH), 126.73 (Ar CH quat), 126.83 (Ar quat), 126.99 (vinylene CH), 127.41 (Ar quat), 127.53 (Ar quat), 127.96 (vinylene CH), 128.01 (vinylene CH), 128.51 (Ar quat), 131.71 (Ar CH), 132.47 (Ar CH), 136.88 (Ar quat), 137.04 (Ar quat), 151.07 (ArO quat), 151.16 (ArO quat), 151.45 (ArO quat), 151.51 (ArO quat) ppm. HRMS calc. for C₅₅H₇₁NO₄Br: 888.4566 g/mol. Found: 888.4586 g/mol.



4-(4-(4-(4-(4-(4-(4-bromostyryl)-2,5-bishexyloxystyryl)styryl)-2,5-bishexyloxybenzonitrile (Br-ABA³-CN). According to the general HWE procedure, Br-ABA³-CHO (200 mg, 0.341 mmol), P-B³-CN (4) (220 mg, 0.517 mmol), and LiCl (34.0 mg, 0.802 mmol) were dissolved in THF (5 mL) and cooled to 0 °C under N₂. KO'Bu (88.0 mg, 0.784 mmol) was added portionwise over 5 minutes, and the reaction was allowed to come to rt overnight with stirring. After workup, column chromatography (silica gel, 2:3 hexanes:DCM) gave the title compound as an orange solid (268 mg, 88%). ¹H NMR (CD₂Cl₂, 400 MHz) δ 0.85-1.00 (12H, mult), 1.30-1.45 (16H, mult), 1.45-1.60 (8H, mult), 1.80-1.95 (8H, mult), 3.99 (2H, t, *J* = 6.4 Hz, OCH₂), 4.07 (4H, t, *J* = 6.4 Hz, OCH₂), 4.11 (2H, t, *J* = 6.4 Hz, OCH₂), 7.05 (1H, s), 7.05 (1H, d, *J* = 16.4 Hz, *trans* CH=CH), 7.26 (1H, d, *J* = 16.4 Hz, *trans* CH=CH), 7.42 (2H, d, *J* = 8.4 Hz, *p*-C₆H₄), 7.48 (1H, d, *J* = 16.4 Hz, *trans* CH=CH), 7.50 (1H, d, *J* = 16.4 Hz, *trans* CH=CH), 7.50 (1H, d, *J* = 8.4 Hz, *p*-C₆H₄), 7.50 (1H, d, *J* = 16.4 Hz, *trans* CH=CH), 7.50 (4H, br s, *p*-C₆H₄), ppm. ¹³C NMR (CD₂Cl₂, 100 MHz) δ 14.39 (CH₃), 14.41 (CH₃), 23.17 (CH₂), 23.20 (CH₂), 23.25 (CH₂), 26.13 (CH₂), 26.40

(CH₂), 26.54 (CH₂), 29.64 (CH₂), 29.74 (CH₂), 30.02 (CH₂), 30.04 (CH₂), 32.10 (CH₂), 32.15 (CH₂), 32.22 (CH₂), 32.23 (CH₂), 70.04 (OCH₂), 70.05 (OCH₂), 70.13 (OCH₂), 70.23 (OCH₂), 100.81 (ArCN, quat), 110.54 (Ar CH), 110.85 (Ar CH), 110.97 (Ar CH), 117.03 (Ar CH), 117.27 (CN), 121.50 (ArBr quat), 122.47 (vinylene CH), 124.17 (vinylene CH), 124.67 (vinylene CH), 127.05 (Ar quat), 127.41 (Ar CH), 127.78 (Ar CH), 127.96 (vinylene CH), 128.52 (Ar CH), 128.75 (vinylene CH), 132.27 (Ar CH, 133.29 (Ar quat), 136.83 (Ar quat), 137.57 (Ar quat), 138.60 (Ar quat), 150.76 (ArO quat), 151.71 (ArO quat), 151.72 (ArO quat), 155.71 (ArO quat) ppm. HRMS calc. for $C_{55}H_{71}NO_4Br$: 888.4566 g/mol. Found: 888.4570 g/mol.



4-(4-(4-(4-bromo-2,5-bishexyloxystyryl)styryl)-2,5-bishexyloxybenzonitrile (Br-BAAB'-CN). According to the general HWE procedure, Br-BAA'-CHO (200 mg, 0.341 mmol), P-B'-CN (4) (220 mg, 0.517 mmol), and LiCl (34.0 mg, 0.802 mmol) were dissolved in THF (5 mL) and cooled to 0 °C under N₂. KO'Bu (88.0 mg, 0784 mmol) was added portionwise over 5 minutes, and the reaction was allowed to come to rt overnight with stirring. After workup, column chromatography (silica gel, 7:3 hexanes:DCM) gave the title compound as an orange solid (270 mg, 89%). ¹H NMR (CD₂Cl₂, 400 MHz) δ 0.85-1.00 (12H, mult), 1.30-1.45 (16H, mult), 1.45-1.60 (8H, mult), 1.80-1.95 (8H, mult), 3.97 (2H, t, *J* = 6.4 Hz, OCH₂), 3.99 (2H, t, *J* = 6.4 Hz, OCH₂), 4.04 (2H, t, *J* = 6.4 Hz, OCH₂), 4.11 (2H, t, *J* = 6.4 Hz, OCH₂), 7.04 (1H, s), 7.11 (1H, s), 7.16 (1H, d, *J* = 16.4 Hz, *trans* CH=CH), 7.16 (1H, d, *J* = 16.4 Hz, *trans* CH=CH), 7.44 (1H, d,

CH=CH), 7.48 (1H, d, J = 16.4 Hz, *trans* CH=CH), 7.54 (4H, br s, *p*-C₆H₄), 7.56 (4H, br s, *p*-C₆H₄) ppm. ¹³C NMR (CD₂Cl₂, 100 MHz) δ 14.40 (CH₃), 23.17 (CH₂), 23.21 (CH₂), 23.22 (CH₂), 26.13 (CH₂), 26.27 (CH₂), 26.40 (CH₂), 26.43 (CH₂), 29.65 (CH₂), 29.73 (CH₂), 29.85 (CH₂), 29.86 (CH₂), 32.10 (CH₂), 32.15 (CH₂), 32.17 (CH₂), 70.13 (OCH₂), 70.22 (OCH₂), 70.24 (OCH₂), 70.72 (OCH₂), 100.85 (ArCN, quat), 110.59 (Ar CH), 111.85 (Ar CH), 112.21 (ArBr quat), 117.02 (Ar CH), 117.26 (CN), 118.32 (Ar CH), 122.63 (vinylene CH), 122.43 (vinylene CH), 127.05 (Ar quat), 127.44 (Ar CH), 127.80 (Ar CH), 128.43 (vinylene CH), 129.04 (vinylene CH), 129.32 (vinylene CH), 132.21 (vinylene CH), 133.24 (Ar quat), 137.02 (Ar quat), 137.16 (Ar quat), 137.81 (Ar quat), 137.98 (Ar quat), 150.36 (ArO quat), 150.77 (ArO quat), 151.67 (ArO quat), 155.71 (ArO quat) ppm. HRMS calc. for C₅₅H₇₁NO₄Br: 888.4566 g/mol.



4-(4-(4-(4-bromo-2,5-bishexyloxystyryl)styryl)-2,5-bishexyloxystyryl)benzonitrile (Br-BABA'-CN). According to the general HWE procedure, Br-BAB'-CHO (300 mg, 0.380 mmol), P-A'-CN (3) (130 mg, 0.577 mmol), and LiCl (37.0 mg, 0.873 mmol) were dissolved in THF (5 mL) and cooled to 0 °C under N₂. KO'Bu (98.0 mg, 0.873 mmol) was added portionwise over 5 minutes, and the reaction was allowed to come to rt overnight with stirring. After workup, column chromatography (silica gel, 1:1 hexanes:DCM) gave the title compound as an orange solid (337 mg, 100%). ¹H NMR (CD₂Cl₂, 400 MHz) δ 0.85-1.00 (12H, mult), 1.30-1.45 (16H, mult), 1.45-1.60 (8H, mult), 1.80-1.95 (8H, mult), 3.97 (2H, t, *J* = 6.4 Hz, OCH₂), 4.04 (2H, t, *J*

= 6.4 Hz, OCH₂), 4.07 (2H, t, J = 6.4 Hz, OCH₂), 4.08 (2H, t, J = 6.4 Hz, OCH₂), 7.11 (1H, s), 7.14 (1H, s), 7.16 (1H, d, J = 16.4 Hz, *trans* CH=CH), 7.17 (1H, s), 7.18 (1H, d, J = 16.4 Hz, *trans* CH=CH), 7.18 (1H, s), 7.20 (1H, d, J = 16.4 Hz, *trans* CH=CH), 7.44 (1H, d, J = 16.4 Hz, *trans* CH=CH), 7.53 (1H, d, J = 16.4 Hz, *trans* CH=CH), 7.55 (4H, br s, *p*-C₆H₄), 7.62 (2H, s, J= 8.8 Hz, *p*-C₆H₄), 7.62 (1H, d, J = 16.4 Hz, *trans* CH=CH), 7.65 (2H, s, J = 8.8 Hz, *p*-C₆H₄) ppm. ¹³C NMR (CD₂Cl₂, 100 MHz) δ 14.40 (CH₃), 23.21 (CH₂), 23.25 (CH₂), 26.27 (CH₂), 26.43 (CH₂), 26.53 (CH₂), 26.54 (CH₂), 29.86 (CH₂), 29.99 (CH₂), 30.03 (CH₂), 32.14 (CH₂), 32.17 (CH₂), 32.21 (CH₂), 32.23 (CH₂), 70.00 (OCH₂), 70.08 (OCH₂), 70.22 (OCH₂), 70.71 (OCH₂), 110.75 (Ar CH), 111.21 (Ar CH), 111.81 (Ar CH), 112.15 (ArBr quat, ArCN quat), 118.33 (Ar CH), 119.62 (CN), 123.28 (vinylene CH), 123.57 (vinylene CH), 126.16 (Ar quat), 127.03 (Ar quat), 127.21 (vinylene CH), 127.30 (Ar CH), 127.40 (Ar CH), 137.62 (Ar quat), 137.77 (Ar quat), 150.36 (ArO quat), 151.60 (ArO quat), 151.66 (ArO quat), 152.06 (ArO quat) ppm. HRMS calc. for C₅₅H₇₁NO₄Br: 888.4566 g/mol. Found: 888.4586 g/mol.



4-(4-(4-(4-bromo-2,5-bishexyloxystyryl)-2,5-bishexyloxystyryl)styryl)benzonitrile (Br-BBAA'-CN). According to the general HWE procedure, Br-BBA'-CHO (300 mg, 0.380 mmol), P-A'-CN (3) (130 mg, 0.577 mmol), and LiCl (37.0 mg, 0.873 mmol) were dissolved in THF (5 mL) and cooled to 0° C under N₂. KO'Bu (98.0 mg, 0.873 mmol) was added portionwise over 5 minutes, and the reaction was allowed to come to rt overnight with stirring. After workup,

Supporting information

column chromatography (silica gel, 1:1 hexanes:DCM) gave the title compound as an orange solid (338 mg, 100%). ¹H NMR (CD₂Cl₂, 400 MHz) & 0.85-1.00 (12H, mult), 1.30-1.45 (16H, mult), 1.45-1.60 (8H, mult), 1.80-1.95 (8H, mult), 3.97 (2H, t, J = 6.4 Hz, OCH₂), 4.04 (2H, t, J = 6.4 Hz, OCH₂), 4.07 (4H, t, J = 6.4 Hz, OCH₂), 7.11 (1H, s), 7.14 (1H, d, J = 16.0 Hz, trans CH=CH), 7.16 (2H, br s), 7.18 (1H, d, J = 16.4 Hz, trans CH=CH), 7.18 (1H, s), 7.25 (1H, d, J = 16.0 Hz, trans CH=CH), 7.44 (1H, d, J = 16.8 Hz, trans CH=CH), 7.50 (1H, d, J = 16.8 Hz, *trans* CH=CH), 7.54 (1H, d, J = 16.4 Hz, *trans* CH=CH), 7.56 (4H, br s, p-C₆H₄), 7.61 (2H, s, J $= 8.4 \text{ Hz}, p-C_6H_4), 7.65 \text{ (2H, s, } J = 8.4 \text{ Hz}, p-C_6H_4) \text{ ppm}.$ ¹³C NMR (CD₂Cl₂, 100 MHz) δ 14.40 (CH₃), 14.42 (CH₃), 14.43 (CH₃), 23.20 (CH₂), 23.23 (CH₂), 23.25 (CH₂), 23.26 (CH₂), 26.28 (CH₂), 26.41 (CH₂), 26.50 (CH₂), 26.55 (CH₂), 29.86 (CH₂), 30.04 (CH₂), 32.14 (CH₂), 32.18 (CH₂), 32.24 (CH₂), 70.00 (OCH₂), 69.96 (OCH₂), 69.97 (OCH₂), 70.13 (OCH₂), 70.65 (OCH₂), 110.83 (Ar CH), 110.96 (Ar CH), 111.03 (ArCN guat), 111.85 (Ar CH), 111.93 (ArBr guat), 118.25 (Ar CH), 119.53 (CN), 123.61 (vinylene CH), 124.42 (vinylene CH), 124.52 (vinylene CH), 126.91 (vinylene CH), 127.07 (Ar quat), 127.36 (Ar CH), 127.41 (Ar CH), 127.66 (Ar quat), 127.85 (Ar CH), 127.89 (Ar quat), 128.51 (vinylene CH), 132.38 (vinylene CH), 136.06 (Ar guat), 138.92 (Ar guat), 142.43 (Ar guat), 150.33 (ArO guat), 151.62 (ArO guat), 151.73 (ArO quat) ppm. HRMS calc. for C₅₅H₇₁NO₄Br: 888.4566 g/mol. Found: 888.4573 g/mol.



4-(4-(4-(4-bromostyryl)styryl)-2,5-bis(hexyloxy)styryl)-2,5-bis(hexyloxy)benzaldehyde (Br-AABB'-CHO). According to the general DIBAL-H procedure, Br-AABB'-CN (1.1347 g, 1.20

Supporting information

mmol) was dissolved in DCM (10 mL) and cooled to 0 $^{\circ}$ C. DIBAL-H (1.0M in hexanes, 1.60 mL, 1.60 mmol) was added dropwise. After workup, column chromatography (silica gel, 7:3 hexanes:DCM) gave the title compound as an orange solid (675.3 mg, 63%).1H NMR (400 MHz, CDCl3) δ 10.38 (s, 1H), 7.57 – 7.37 (m, 9H), 7.32 (d, J = 8.5 Hz, 3H), 7.16 – 6.92 (m, 6H), 4.12 – 3.90 (m, 8H), 1.91 – 1.70 (m, 8H), 1.57 – 1.39 (m, 8H), 1.39 – 1.22 (m, 16H), 1.00 – 0.71 (m, 12H). 13C NMR (100 MHz, CD₂Cl₂) δ 189.06, 156.60, 151.77, 151.47, 151.08, 151.08, 137.95, 136.80, 136.62, 135.17, 135.17, 132.14, 129.34, 128.88, 128.36, 127.76, 127.43, 127.28, 127.24, 127.05, 124.50, 123.69, 123.15, 121.53, 111.04, 110.77, 110.59, 110.21, 69.82, 69.77, 69.59, 69.51, 32.03, 31.99, 31.94, 29.83, 29.62, 26.35, 26.31, 26.24, 26.16, 23.07, 23.05, 22.98, 14.21, 14.21, 14.18, 14.18. HRMS calc. for C₅₅H₇₂O₅Br: 891.4563 g/mol. Found: 888.4579 g/mol.



4-(4-(4-(4-bromo-2,5-bis(hexyloxy)styryl)styryl)-2,5-bis(hexyloxy)styryl)benzaldehyde (Br-BABA'-CHO). According to the general DIBAL-H procedure, Br-BABA'-CN (1.3587 g, 1.50 mmol) was dissolved in DCM (15 mL) and cooled to 0 ^oC. DIBAL-H (1.0M in hexanes, 1.90 mL, 1.90 mmol) was added dropwise. After workup, column chromatography (silica gel, 7:3 hexanes:DCM) gave the title compound as an orange solid (1.2502 g, 93%).¹H NMR (400 MHz, CDCl₃) δ 10.00 (s, 1H), 7.87 (d, J = 8.2 Hz, 2H), 7.66 (m, 3H), 7.57 – 7.46 (m, 5H), 7.42 (d, J = 16.4 Hz, 1H), 7.15 (m 7H), 4.04 (m, 8H), 1.98 – 1.78 (m, 8H), 1.64 – 1.47 (m, 8H), 1.47 – 1.31 (m, 16H), 1.00 – 0.83 (m, 12H).¹³C NMR (100 MHz, CD₂Cl₂) δ 191.76, 151.86, 151.47, 151.43,

150.17, 144.42, 137.61, 137.40, 135.61, 130.43, 129.19, 129.11, 128.10, 127.62, 127.21, 127.15, 126.85, 126.25, 123.42, 123.07, 118.15, 111.95, 111.63, 111.00, 110.58, 70.53, 70.03, 69.89, 69.83, 32.03, 32.02, 31.96, 31.94, 29.83, 29.80, 29.66, 26.34, 26.23, 26.06, 23.05, 23.01, 23.00, 14.20. HRMS calc. for C₅₅H₇₂O₅BrNa: 913.4383 g/mol. Found: 913.4297 g/mol.



4-(4-(4-(4-bromo-2,5-bis(hexyloxy)styryl)-2,5-bis(hexyloxy)styryl)styryl)benzaldehyde (Br-BBAA'-CHO). According to the general DIBAL-H procedure, Br-BBAA'-CN (1.3952 g, 1.60 mmol) was dissolved in DCM (15 mL) and cooled to 0 $^{\circ}$ C. DIBAL-H (1.0M in hexanes, 2.00 mL, 2.00 mmol) was added dropwise. After workup, column chromatography (silica gel, 7:3 hexanes:DCM) gave the title compound as an orange solid (1.2957 g, 91%).¹HNMR(300MHz, CDCl₃) 10.00 (s, 1H), 7.89-7.86 (d, *J*= 9 Hz, 2H), 7.68-7.65 (d, *J*=9 Hz, 2H), 7.56-7.50 (m, 5H), 7.44-7.42 (d, *J*= 6 Hz, 2H), 7,25-7.08 (m, 7H), 4.08-3.94 (m, 8H), 1.91-1.82 (m, 8H), 1.56-1.51 (m, 8H), 1.43-1.36 (m, 16H), 0.94-0.87 (m, 12H). ¹³C NMR (100 MHz, CD₂Cl₂) δ 191.75, 151.53, 151.43, 150.14, 143.76, 138.61, 136.12, 135.77, 131.99, 130.44, 128.37, 127.63, 127.48, 127.32, 127.20, 126.92, 124.34, 124.14, 123.41, 118.06, 111.67, 110.79, 110.63, 70.47, 69.95, 69.77, 32.03, 31.97, 31.93, 29.83, 29.66, 26.35, 26.30, 26.20, 26.07, 23.04, 23.03, 22.99, 14.20, 14.18. HRMS calc. for C₅₅H₇₂O₅BrNa: 913.4383 g/mol. Found: 913.4302 g/mol.



4-(4-(4-(4-(4-bromostyryl)styryl)-2,5-bis(hexyloxy)styryl)-2,5-bis(hexyloxy)styryl)-2,5-

bis(hexyloxy)benzonitrile (**Br-AABBB'-CN).** According to the general HWE procedure, Br-AABB' -CHO (546.7 mg, 0.61 mmol), P-B'-CN (4) (387.2 mg, 0.91 mmol), and LiCl (59.6 mg, 1.41 mmol) were dissolved in THF (10 mL) and cooled to 0 °C under N₂. KO'Bu (157.4 mg, 1.41 mmol) was added portionwise over 5 minutes, and the reaction was allowed to come to rt overnight with stirring. After workup, column chromatography (silica gel, 7:3 hexanes: DCM) gave the title compound as an orange solid (669.3 mg, 93%). ¹H NMR (400 MHz, CDCl3) δ 7.60 – 7.44 (m, 10H), 7.40 (t, *J* = 7.5 Hz, 3H), 7.17 (d, *J* = 1.6 Hz, 4H), 7.13 (d, *J* = 4.1 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.00 (q, *J* = 6.7 Hz, 2H), 4.13 – 3.93 (m, 12H), 1.92 – 1.79 (m, 12H), 1.61 – 1.46 (m, 12H), 1.43 – 1.29 (m, 24H), 0.99 – 0.83 (m, 18H).¹³C NMR (100 MHz, CD₂Cl₂) δ 155.52, 151.77, 151.50, 150.49, 136.79, 133.83, 132.12, 129.34, 128.58, 128.34, 127.72, 127.35, 127.26, 127.17, 124.13, 124.11, 121.50, 117.15, 116.75, 111.02, 110.63, 110.46, 110.32, 110.26, 100.27, 78.08, 69.93, 69.77, 69.66, 32.04, 31.95, 31.88, 29.84, 29.53, 29.43, 26.35, 26.32, 26.18, 25.93, 23.05, 23.01, 22.95, 14.20, 14.16. HRMS calc. for C₇₅H₁₀₁NO₆Br: 1190.6812 g/mol. Found: 1190.6786 g/mol.



4-(4-(4-(4-(4-bromo-2,5-bis(hexyloxy)styryl)styryl)-2,5-bis(hexyloxy)styryl)-2,5-

bis(hexyloxy)benzonitrile (Br-BABA'-CN). According to the general HWE procedure, Br-BABA'-CHO (300 mg, 0.380 mmol), P-B'-CN (4) (1.1465 g, 1.3 mmol), and LiCl (127.5 mg, 3.0 mmol) were dissolved in THF (17 mL) and cooled to 0 °C under N₂. KO'Bu (336.6 mg, 3.0 mmol) was added portionwise over 5 minutes, and the reaction was allowed to come to rt overnight with stirring. After workup, column chromatography (silica gel, 7:3 hexanes: DCM) gave the title compound as an orange solid (1.5040 g, 97%). ¹H NMR (400 MHz, CDCl₃) δ 7.58 – 7.37 (m, 12H), 7.13 (m, 10H), 4.15 – 3.92 (m, 12H), 1.95 – 1.77 (m, 12H), 1.64 – 1.47 (m, 12H), 1.46 – 1.29 (m, 24H), 1.01 – 0.80 (m, 18H). ¹³C NMR (100 MHz, CDCl₃) δ 155.24, 151.19, 151.13, 151.10, 150.14, 149.81, 138.12, 137.30, 136.88, 136.10, 132.87, 131.85, 128.95, 128.46, 128.12, 127.23, 127.12, 126.85, 126.73, 126.58, 123.85, 123.28, 122.77, 121.95, 117.83, 116.82, 116.46, 111.86, 111.56, 110.55, 110.48, 110.09, 100.38, 70.30, 69.67, 69.60, 31.64, 31.56, 31.51, 29.47, 29.28, 29.15, 29.07, 25.97, 25.85, 25.82, 25.70, 25.58, 22.66, 22.61, 22.57, 14.05, 14.03. HRMS calc. for C₇₅H₁₀₀NO₆Br+Na: 1212.6632 g/mol. Found: 1212.6569 g/mol.



4-(4-(4-(4-(4-bromo-2,5-bis(hexyloxy)styryl)-2,5-bis(hexyloxy)styryl)styryl)styryl) benzonitrile (Br-BBAAA'-CN). According to the general HWE procedure, Br-BBAA'-CHO

(1.1539 mg, 1.3 mmol), P-A'-CN (3) (450.4 mg, 2.0 mmol), and LiCl (127.5 mg, 3.0 mmol) were dissolved in THF (16 mL) and cooled to 0 °C under N₂. KO'Bu (336.6 mg, 3.0 mmol) was added portionwise over 5 minutes, and the reaction was allowed to come to rt overnight with stirring. After workup, column chromatography (silica gel, 7:3 hexanes: DCM) gave the title compound as an orange solid (1.2552 g, 97%). ¹H NMR (400 MHz, CDCl₃) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.56 – 7.48 (m, 9H), 7.42 (t, *J* = 13.5 Hz, 2H), 7.25 – 7.04 (m, 9H), 4.11 – 3.93 (m, 8H), 1.96 – 1.78 (m, 8H), 1.64 – 1.47 (m, 8H), 1.44 – 1.29 (m, 16H), 1.02 – 0.84 (m, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 151.15, 151.06, 151.03, 149.81, 141.83, 137.79, 137.63, 136.22, 135.50, 132.48, 131.94, 128.92, 128.22, 127.65, 127.37, 127.31, 127.23, 126.91, 126.86, 126.81, 126.43, 123.99, 123.57, 123.03, 119.04, 117.78, 111.62, 111.55, 110.61, 110.48, 70.21, 69.54, 69.48, 31.64, 31.58, 29.45, 29.29, 25.97, 25.92, 25.82, 25.71, 22.65, 22.63, 22.60, 14.05. HRMS calc. for C₆₃H₇₆NO₄Br+Na: 1012.4855 g/mol. Found: 1012.4783 g/mol.



24H), 1.06 – 0.76 (m, 18H). ¹³C NMR (100 MHz, CD₂Cl₂) δ 188.86, 156.65, 151.84, 151.58 151.53, 151.44, 151.11, 131.96, 129.22, 128.91, 128.30, 128.18, 127.20, 127.17, 127.10, 127.01, 123.94, 123.68, 123.51, 122.82, 110.87, 110.62, 110.58, 110.55, 110.43, 110.10, 69.69, 69.64, 69.57, 69.46, 69.38, 54.08, 53.81, 53.53, 31.88, 31.86, 31.82, 31.76, 29.88, 29.69, 29.45, 26.19, 26.15, 26.07, 25.98, 22.88, 22.79, 14.02, 13.98. HRMS calc. for C₇₅H₁₀₂O₇Br: 1193.6809 g/mol. Found: 1193.6865 g/mol.



4-(4-(4-(4-(4-bromo-2,5-bis(hexyloxy)styryl)styryl)-2,5-bis(hexyloxy)styryl)-2,5-

bis(hexyloxy)benzaldehyde (Br-BABAB'-CHO). According to the general DIBAL-H procedure, Br-BABAB'-CN (600.0 mg, .050 mmol) was dissolved in DCM (5 mL) and cooled to 0 $^{\circ}$ C. DIBAL-H (1.0M in hexanes, 0.65 mL, 0.65 mmol) was added dropwise. After workup, column chromatography (silica gel, 7:3 hexanes:DCM) gave the title compound as an orange solid (517.1 mg, 87%).¹H NMR (400 MHz, CDCl₃) δ 10.62 – 10.33 (m, 1H), 7.57 – 7.46 (m, 11H), 7.42 (d, *J* = 16.4 Hz, 1H), 7.31 (d, *J* = 24.7 Hz, 2H), 7.24 – 7.07 (m, 8H), 4.26 – 3.85 (m, 12H), 2.06 – 1.75 (m, 12H), 1.56 (m, 12H), 1.46 – 1.31 (m, 24H), 1.00 – 0.86 (m, 18H). ¹³C NMR (100 MHz, CD₂Cl₂) δ 189.06, 156.58, 151.56, 151.51, 151.47, 151.12, 150.17, 138.37, 137.74, 137.29, 136.82, 134.48, 132.07, 129.22, 128.66, 128.46, 127.59, 127.28, 127.21, 127.18, 127.04, 126.88, 124.65, 123.97, 123.55, 122.99, 122.81, 118.14, 111.93, 111.62, 110.82, 110.68, 110.63, 110.29, 70.53, 70.04, 69.88, 69.66, 69.59, 32.06, 31.98, 31.96, 29.87, 29.67, 29.62,

26.37, 26.27, 26.25, 26.15, 26.08, 23.07, 23.03, 23.02, 23.00, 14.24, 14.21. HRMS calc. for C₇₅H₁₀₁O₇Br+Na: 1215.6628 g/mol. Found: 1215.6561 g/mol.



4-(4-(4-(4-(4-bromo-2,5-bis(hexyloxy)styryl)-2,5-bis(hexyloxy)styryl)styryl)

benzaldehyde (**Br-BBAAA'-CHO).** According to the general DIBAL-H procedure, Br-BBAAA'-CN (601.8 mg, 0.60 mmol) was dissolved in DCM (7 mL) and cooled to 0 $^{\circ}$ C. DIBAL-H (1.0M in hexanes, 0.80 mL, 0.80 mmol) was added dropwise. After workup, column chromatography (silica gel, 7:3 hexanes:DCM) gave the title compound as an orange solid (500.1 mg, 84%).¹H NMR (400 MHz, CDCl₃) δ 10.00 (s, 1H), 7.88 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.59 – 7.47 (m, 9H), 7.42 (t, *J* = 13.6 Hz, 2H), 7.27 (d, *J* = 16.3 Hz, 1H), 7.20 – 7.04 (m, 8H), 4.14 – 3.89 (m, 8H), 2.01 – 1.78 (m, 8H), 1.64 – 1.45 (m, 8H), 1.45 – 1.28 (m, 16H), 1.02 – 0.77 (m, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 191.57, 151.15, 151.06, 151.04, 149.81, 143.43, 137.66, 137.60, 136.27, 135.79, 135.27, 131.75, 130.25, 128.83, 128.24, 127.73, 127.37, 127.30, 127.25, 127.08, 126.91, 126.87, 126.81, 123.55, 123.03, 117.79, 111.62, 110.62, 70.22, 69.49, 31.64, 31.56, 29.46, 29.29, 25.98, 25.92, 25.83, 25.71, 22.66, 22.64, 22.60, 14.04. HRMS calc. for C₆₃H₇₇O₅Br+Na: 1015.4852 g/mol. Found: 1015.4802 g/mol.



4-(4-(4-(4-(4-(4-(4-(bromostyryl)styryl)-2,5-bis(hexyloxy)styryl)-2,5-bis(hexyloxy)styryl)benzonitrile (**Br-AABBBA'-CN).** According to the general HWE procedure, Br-AABBB'-CHO (141.7 mg, 0.12 mmol), P-A'-CN (3) (81.1 mg, 0.36 mmol), and LiCl (11.4 mg, 0.27 mmol) were dissolved in THF (10 mL) and cooled to 0 °C under N₂. KO'Bu (30.3 mg, 0.27 mmol) was added portionwise over 5 minutes, and the reaction was allowed to come to rt overnight with stirring. After workup, column chromatography (silica gel, 7:3 hexanes: DCM) gave the title compound as an orange solid (147.0 mg, 92%). ¹H NMR (400 MHz, CD2Cl2) δ 7.66 – 7.30 (m, 18H), 7.19 – 6.96 (m, 10H), 3.99 (d, *J* = 6.1 Hz, 12H), 1.87 – 1.72 (m, 12H), 1.47 (d, *J* = 17.0 Hz, 12H), 1.39 – 1.22 (m, 24H), 0.97 – 0.69 (m, 18H). ¹³C NMR (100 MHz, CD₂Cl₂) δ 151.86, 151.86, 151.50, 151.50, 142.92, 138.11, 138.08, 138.07, 136.80, 136.48, 132.83, 132.12, 129.35, 128.34, 127.88, 127.44, 127.43, 127.32, 127.26, 127.17, 127.08, 126.86, 125.76, 123.72, 121.49, 119.45, 110.94, 110.58, 110.50, 69.79, 69.72, 32.06, 32.00, 30.42, 30.05, 29.86, 29.79, 26.34, 23.07, 23.03, 14.24, 14.22, 14.19. HRMS calc. for C₈₃H₁₀₇NO₆Br: 1292.7282 g/mol. Found: 1292.7290 g/mol.



4-(4-(4-(4-(4-(4-(4-bromo-2,5-bis(hexyloxy)styryl)styryl)-2,5-bis(hexyloxy)styryl)benzonitrile (Br-BABABA'-CN). According to the general HWE

procedure, Br-BABAB'-CHO (300.0 mg, 0.25 mmol), P-A'-CN (3) (85.6 mg, 0.38 mmol), and LiCl (24.7 mg, 0.58 mmol) were dissolved in THF (5 mL) and cooled to 0 °C under N₂. KO'Bu (65.1 mg, 0.58 mmol) was added portionwise over 5 minutes, and the reaction was allowed to come to rt overnight with stirring. After workup, column chromatography (silica gel, 7:3 hexanes: DCM) gave the title compound as an orange solid (273.2 mg, 84.5%). ¹H NMR (400 MHz, CDCl₃) δ 7.68 – 7.56 (m, 5H), 7.51 (m, 11H), 7.41 (d, *J* = 16.4 Hz,1H), 7.22 – 7.02 (m, 11H), 4.16 – 3.92 (m, 12H), 1.99 – 1.78 (m, 12H), 1.70 – 1.46 (m, 12H), 1.39 (dd, *J* = 6.1, 2.8 Hz, 24H), 1.10 – 0.83 (m, 18H).¹³C NMR (100 MHz, CD₂Cl₂) δ 151.86, 151.50, 150.16, 150.16, 142.88, 137.72, 132.82, 129.25, 127.15, 127.15, 127.10, 127.10, 123.54, 123.53, 118.14, 111.90, 111.61, 111.03, 110.55, 110.55, 109.67, 70.52, 70.52, 70.03, 69.88, 69.88, 69.81, 54.33, 54.06, 53.79, 53.52, 53.25, 32.03, 31.99, 31.95, 29.85, 29.64, 26.34, 26.22, 26.05, 23.05, 23.00, 14.21, 14.18. HRMS calc. for C₈₃H₁₀₆NO₆Br+Na: 1314.7101 g/mol. Found: 1314.7034 g/mol.



4-(4-(4-(4-(4-(4-(4-(4-bromo-2,5-bis(hexyloxy)styryl)-2,5-bis(hexyloxy)styryl)styryl)styryl)styryl) 2,5-bis(hexyloxy)benzonitrile (**Br-BBAAAB'-CN).** According to the general HWE procedure, Br-BBAAA'-CHO (300 mg, 0.30 mmol), P-B'-CN (4) (191.3 mg, 0.45 mmol), and LiCl (29.3 mg, 0.69 mmol) were dissolved in THF (10 mL) and cooled to 0 °C under N₂. KO'Bu (77.4 mg, 0.69 mmol) was added portionwise over 5 minutes, and the reaction was allowed to come to rt overnight with stirring. After workup, column chromatography (silica gel, 7:3 hexanes: DCM) gave the title compound as an orange solid (280.3 mg, 72.2%). ¹H NMR (400

MHz, CDCl₃) δ 7.62 – 7.35 (m, 16H), 7.26 – 7.00 (m, 12H), 4.03 (m, 12H), 1.96 – 1.76 (m, 12H), 1.53 (d, J = 5.8 Hz, 12H), 1.37 (s, 24H), 1.06 – 0.81 (m, 18H).¹³C NMR (100 MHz, CDCl₃) δ 155.24, 151.14, 151.06, 151.03, 150.15, 149.81, 137.47, 137.41, 136.93, 136.51, 136.40, 136.35, 132.81, 131.77, 128.61, 128.37, 128.27, 127.90, 127.34, 127.26, 126.90, 126.85, 124.00, 123.46, 123.01, 122.16, 117.79, 116.80, 116.46, 111.60, 110.62, 110.48, 110.13, 100.44, 70.21, 69.67, 69.49, 31.65, 31.56, 31.54, 31.51, 29.48, 29.29, 29.14, 29.06, 25.98, 25.92, 25.81, 25.71, 25.58, 22.66, 22.64, 22.60, 22.57, 14.04. HRMS calc. for C₈₃H₁₀₇NO₆Br: 1292.7282 g/mol. Found: 1292.7288 g/mol.

CYCLIC AND DIFFERENTIAL PULSE VOLTAMMOGRAMS OF OLIGOMERS

Oligomer	$E_{ m peak}^{ m Oxd}$ "/ V	$E_{ m peak}^{ m Red}$ ^a / V
Br-AA'-CN	1.45	-1.93, -2.07
Br-BA'-CN	1.06, 1.15	-1.96, -2.07
Br-AB'-CN	1.23, 1.34	-1.94, -2.07
Br-BB'-CN	1.06, 1.36	-2.17
Br-AAB'-CN	1.06, 1.30	-1.94,-2.18
Br-BAA'-CN	0.95, 1.15, 1.44	-1.93, -2.18
Br-BAB'-CN	0.97, 1.18, 1.32	-1.97, -2.23
Br-ABA'-CN	0.84, 1.23	-1.92, -2.16
Br-ABB'-CN	0.81, 1.02, 1.24	-1.93, -2.16
Br-BBA'-CN	0.78, 1.04, 1.24, 1.41	-1.94, -2.17
Br-BAAB'-CN	0.87, 1.02, 1.19, 1.39	-1.94, -2.04, -2.27, -2.49, -2.7, -2.83
Br-ABAB'-CN	0.69, 1.13, 1.24	-2.02, -2.31, -2.58, -2.76, -2.87
Br-BABA'-CN	0.69, 0.98, 1.18	-1.98, -2.11, -2.33, -2.53, -2.66, -2.84
Br-BBAA'-CN	0.65, 0.83, 0.97, 1.04, 1.19, 1.36	-1.99, -2.11, -2.29, -2.53, -2.80
Br-AABB'-CN	0.70, 1.01, 1.14, 1.34	-1.99, -2.31, -2.63, -2.81
Br-ABBA'-CN	0.67, 0.87, 0.97, 1.04, 1.23	-1.95, -2.14, -2.24, -2.45, -2.59, -2.75
Br-AABBB'-CN	0.63, 0.74, 0.85, 0.98,1.18, 1.39	-1.97, -2.17, -2.27, -2.44, -2.64
Br-BABAB'-CN	0.7, 0.88, 0.96, 1.08, 1.2, 1.29	-1.96, -2.17, -2.26, -2.42, -2.7, -2.8
Br-BBAAA'-CN	0.69, 0.89, 1.16, 1.22, 1.43	-1.96, -2.11, -2.25, -2.4, -2.67, -2.74, -3.04
Br-AABBBA'-CN	0.54, 0.81, 1.06, 1.27, 1.47	-1.92, -2.12, -2.26, -2.4, -2.65, -2.76, -3.06
Br-BABABA'-CN	0.64, 1.18, 1.26, 1.44	-1.94, -2.14, -2.26, -2.4, -2.67, -2.79, -3.08
Br-BBAAAB'-CN	0.67, 0.86, 0.97, 1.05, 1.3	-1.99, -2.13, -2.42, -2.49, -2.7, -2.87

Table S2. Peak oxidation and reduction potentials of oligomers

^a Potential vs. Ag/Ag⁺, 240µM in 0.1 M Bu₄NPF₆ in THF

Figure S1. Top: Cyclic voltammograms of Br-AA'-CN in THF. Bottom: Differential pulse voltammograms of Br-AA'-CN in THF. Left: reduction. Right: oxidation.



Figure S2. Top: Cyclic voltammograms of Br-AB'-CN in THF. Bottom: Differential pulse voltammograms of Br-AB'-CN in THF. Left: reduction. Right: oxidation.



Figure S3. Top: Cyclic voltammograms of Br-BA'-CN in THF. Bottom: Differential pulse voltammograms of Br-BA'-CN in THF. Left: reduction. Right: oxidation.



Figure S4. Top: Cyclic voltammograms of Br-BB'-CN in THF. Bottom: Differential pulse voltammograms of Br-BB'-CN in THF. Left: reduction. Right: oxidation.



Figure S5. Top: Cyclic voltammograms of Br-AAB'-CN in THF. Bottom: Differential pulse voltammograms of Br-AAB'-CN in THF. Left: reduction. Right: oxidation.



Figure S6. Top: Cyclic voltammograms of Br-ABA'-CN in THF. Bottom: Differential pulse voltammograms of Br-ABA'-CN in THF. Left: reduction. Right: oxidation.



Figure S7. Top: Cyclic voltammograms of Br-ABB'-CN in THF. Bottom: Differential pulse voltammograms of Br-ABB'-CN in THF. Left: reduction. Right: oxidation.



Figure S8. Top: Cyclic voltammograms of Br-BAA'-CN in THF. Bottom: Differential pulse voltammograms of Br-BAA'-CN in THF. Left: reduction. Right: oxidation.



Figure S9. Top: Cyclic voltammograms of Br-BAB'-CN in THF. Bottom: Differential pulse voltammograms of Br-BAB'-CN in THF. Left: reduction. Right: oxidation.



Figure S10. Top: Cyclic voltammograms of Br-BBA'-CN in THF. Bottom: Differential pulse voltammograms of Br-BBA'-CN in THF. Left: reduction. Right: oxidation.



Figure S11. Top: Cyclic voltammograms of Br-AABB'-CN in THF. Bottom: Differential pulse voltammograms of Br-AABB'-CN in THF. Left: reduction. Right: oxidation.



Figure S12. Top: Cyclic voltammograms of Br-ABAB'-CN in THF. Bottom: Differential pulse voltammograms of Br-AABB'-CN in THF. Left: reduction. Right: oxidation.



Supporting information

Figure S13. Top: Cyclic voltammograms of Br-BBAA'-CN in THF. Bottom: Differential pulse voltammograms of Br-BBAA'-CN in THF. Left: reduction. Right: oxidation.



Figure S14. Top: Cyclic voltammograms of Br-BABA'-CN in THF. Bottom: Differential pulse voltammograms of Br-BABA'-CN in THF. Left: reduction. Right: oxidation.



Figure S15. Top: Cyclic voltammograms of Br-ABBA'-CN in THF. Bottom: Differential pulse voltammograms of Br-ABBA'-CN in THF. Left: reduction. Right: oxidation.



Figure S16. Top: Cyclic voltammograms of Br-BAAB'-CN in THF. Bottom: Differential pulse voltammograms of Br-BAAB'-CN in THF. Left: reduction. Right: oxidation.



Figure S17. Top: Cyclic voltammograms of Br-AABBB'-CN in THF. Bottom: Differential pulse voltammograms of Br-AABBB'-CN in THF. Left: reduction. Right: oxidation.


Figure S18. Top: Cyclic voltammograms of Br-BABAB'-CN in THF. Bottom: Differential pulse voltammograms of Br-BABAB'-CN in THF. Left: reduction. Right: oxidation.



Figure S19. Top: Cyclic voltammograms of Br-BBAAA'-CN in THF. Bottom: Differential pulse voltammograms of Br-BBAAA'-CN in THF. Left: reduction. Right: oxidation.



Figure S20. Top: Cyclic voltammograms of Br-AABBBA'-CN in THF. Bottom: Differential pulse voltammograms of Br-AABBBA'-CN in THF. Left: reduction. Right: oxidation.



Figure S21. Top: Cyclic voltammograms of Br-BABABA'-CN in THF. Bottom: Differential pulse voltammograms of Br-BABABA'-CN in THF. Left: reduction. Right: oxidation.



Figure S22. Top: Cyclic voltammograms of Br-BBAAAB'-CN in THF. Bottom: Differential pulse voltammograms of Br-BBAAAB'-CN in THF. Left: reduction. Right: oxidation.



ABSORBANCE AND EMISSION SPECTRA OF OPVS

Oligomer	$\lambda^{abs}_{max} \ {}^{\rm a}/\!{}^{\rm nm}$	ε ^b / 10 ⁻³ cm ⁻¹ M ⁻¹	λ_{max}^{em} "	$\lambda_{max}^{em}{}^{_{c}}/_{nm}$	$\Delta E_{gap}^{opt}\ {}^{\rm d}/{\rm eV}$
Br-AA'-CN	327	54.5	379	463	3.44
Br-BA'-CN	309, 362	28.1, 29.2	450	460	2.97
Br-AB'-CN	316, 364	29.4, 24.9	418	443	2.99
Br-BB'-CN	303, 380	16.9, 26.6	450	519	2.89
Br-AAB'-CN	385	93.2	433	507	2.86
Br-BAA'-CN	383	73.2	476	497	2.84
Br-BAB'-CN	396	72.4	474	504	2.77
Br-ABA'-CN	334, 406	37.9, 50.2	477	514	2.65
Br-ABB'-CN	329, 412	34.0, 53.8	478	524	2.63
Br-BBA'-CN	<u>333, 412</u>	<u>29.4, 53.9</u>	488	522	<u>2.62</u>
Br-BAAB'-CN	408	93.3	485	512	2.72
Br-ABAB'-CN Br-BABA'-CN Br-BABA'-CN	422 425 266 424	73.9 89.9	499 492	549 534	2.58 2.56
Br-AABB'-CN Br-ABBA'-CN	360, 424 360, 425 337, 437	41.4, 80.2 47.9, 83.7 35.3, 78.3	492 511	535 547 541	2.55 2.47
Br-AABBB'-CN	351,449	35.5, 90.7	522	578	2.43
Br-BABAB'-CN	435	97.7	508	557	2.52
Br-BBAAA'-CN	427	78.1	<u>500</u>	583	2.56
Br-AABBBA'-CN	342,462	40.8, 94.0	538	616	2.29
Br-BABABA'-CN	448	112.2	509	580	2.46
Br-BBAAAB'-CN	430	108.0	494	566	2.53

Table S3. Optical properties of sequenced OPVs

^a Measured in chloroform solution ^bcalculated at λ_{max}^{abs} ; ^cThin film, cast from chloroform solution; ^dE_g determined at the onset of the absorption spectrum.



Figure S23. Absorption (in CHCl₃) and emission (in CHCl₃ and film) spectra of Br-AA'-CN.

Figure S24. Absorption (in CHCl₃) and emission (in CHCl₃ and film) spectra of Br-BB'-CN.





Figure S25. Absorption (in CHCl₃) and emission (in CHCl₃ and film) spectra of Br-AB'-CN.

Figure S26. Absorption (in CHCl₃) and emission (in CHCl₃ and film) spectra of Br-BA'-CN.





Figure S27. Absorption (in CHCl₃) and emission (in CHCl₃ and film) spectra of Br-AAB'-CN.

Figure S28. Absorption (in CHCl₃) and emission (in CHCl₃ and film) spectra of Br-BAA'-CN.





Figure S29. Absorption (in CHCl₃) and emission (in CHCl₃ and film) spectra of Br-ABA'-CN.

Figure S30. Absorption (in CHCl₃) and emission (in CHCl₃ and film) spectra of Br-BAB'-CN.





Figure S31. Absorption (in CHCl₃) and emission (in CHCl₃ and film) spectra of Br-ABB'-CN.

Figure S32. Absorption (in CHCl₃) and emission (in CHCl₃ and film) spectra of Br-BBA'-CN.





Figure S33. Absorption (in CHCl₃) and emission (in CHCl₃ and film) spectra of Br-AABB'-CN.

Figure S34. Absorption (in CHCl₃) and emission (in CHCl₃ and film) spectra of Br-ABAB'-CN.





Figure S35. Absorption (in CHCl₃) and emission (in CHCl₃ and film) spectra of Br-BABA'-CN.

Figure S36. Absorption (in CHCl₃) and emission (in CHCl₃ and film) spectra of Br-ABBA'-CN.





Figure S37. Absorption (in CHCl₃) and emission (in CHCl₃ and film) spectra of Br-BAAB'-CN.

Figure S38. Absorption (in CHCl₃) and emission (in CHCl₃ and film) spectra of Br-BBAA'-CN.





Figure S39. Absorption (CHCl₃) and emission (CHCl₃ and film) spectra of Br-AABBB'-CN.

Figure S40. Absorption (CHCl₃) and emission (CHCl₃ and film) spectra of Br-BABAB'-CN.





Figure S41. Absorption (CHCl₃) and emission (CHCl₃ and film) spectra of Br-BBAAA'-CN.

Figure S42. Absorption (CHCl₃) and emission (CHCl₃ and film) spectra of Br-AABBBA'-CN.





Figure S43. Absorption (CHCl₃) and emission (CHCl₃ and film) spectra of Br-BABABA'-CN.

Figure S44. Absorption (CHCl₃) and emission (CHCl₃ and film) spectra of Br-BBAAAB'-CN.



DIFFERENTIAL SCANNING CALORIMOGRAMS OF OLIGOMERS

In figures S45 - S67, the heating curve is plotted in red and the cooling curve in blue.

Oligomer	$T_{iso} \ ^{a}/ \ ^{o}C$	$T_{LC}^{a} / {}^{\circ}C$	$T_C^{b} / °C$
Br-AA'-CN	197		151, 167
Br-BA'-CN	83.2	—	30.6
Br-AB'-CN	74.7 ^c	—	_
Br-BB'-CN	96.3	—	68.8
Br-AAB'-CN	105	—	41.6
Br-BAA'-CN	125 ^c	—	_
Br-BAB'-CN	104	—	77.8
Br-ABA'-CN	185	64.8 ^c	79.5, 85.3, 92.7
Br-ABB'-CN	114	—	43.2
Br-BBA'-CN	109	—	—
Br-BAAB'-CN	119	81.2	—
Br-ABAB'-CN	123	85.0	41.7
Br-BABA'-CN	94	75.4	_
Br-BBAA'-CN	116	111,	57.5
Br-AABB'-CN	144	66.3 ^c	114, 121
Br-ABBA'-CN	191	—	124
Br-AABBB'-CN	169	160	156
Br-BABAB'-CN	130	110	106
Br-BBAAA'-CN	171	86.2 ^c	153
Br-AABBBA'-CN	184	178, 161	165,169
Br-BABABA'-CN	134	92,105	55.3
Br-BBAAAB'-CN	122	_	_

Table S4. Thermal properties of the sequenced OPVs

^a Exothermic transition observed on second heating scan; ^b Exothermic transition observed on second cooling scan; ^c Transition observed in first scan only



Figure S45. DSC thermograms of all six sequenced tetramers and all three sequenced hexamers.

Figure S46. DSC thermograms of Br-AA'-CN.











Figure S48. DSC thermograms of Br-BA'-CN.



Figure S49. DSC thermograms of Br-BB'-CN.



Figure S50. DSC thermograms of Br-AAB'-CN.



Figure S51. DSC thermograms of Br-ABA'-CN.



Figure S52. DSC thermograms of Br-ABB'-CN.



Figure S53. DSC thermograms of Br-BAA'-CN.



Figure S54. DSC thermograms of Br-BAB'-CN.







Figure S56. DSC thermograms of Br-AABB'-CN.



Figure S57. DSC thermograms of Br-ABAB'-CN.



Figure S58. DSC thermograms of Br-ABBA'-CN.



Figure S59. DSC thermograms of Br-BAAB'-CN.



Figure S60. DSC thermograms of Br-BABA'-CN.



Figure S61. DSC thermograms of Br-BBAA'-CN.

Figure S62. DSC thermograms of Br-AABBB'-CN.










Figure S64. DSC thermograms of Br-BBAAA'-CN.





















COMPUTATIONAL RESULTS

Table S5. Computed Orbital Energies (from B3LYP/6-31G*/THF) and Δ SCF Energies.

Compound	HOMO (eV)	LUMO (eV)	ΔSCF(+)	ΔSCF(-)
Br-AA'-CN	-5.930	-2.150	5.905	2.215
Br-BA'-CN	-5.527	-2.096	5.465	2.178
Br-AB'-CN	-5.631	-2.099	5.570	2.200
Br-BB'-CN	-5.390	-2.056	5.315	2.161
Br-AAB'-CN	-5.349	-2.204	5.288	2.298
Br-BAA'-CN	-5.398	-2.252	5.091	2.401
Br-BAB'-CN	-5.181	-2.178	5.087	2.294
Br-ABA'-CN	-5.202	-2.262	5.122	2.369
Br-ABB'-CN	-5.118	-2.116	5.050	2.218
Br-BBA'-CN	-5.096	-2.219	4.995	2.331
Br-BAAB'-CN	-5.150	-2.261	4.906	2.376
Br-ABAB'-CN	-4.999	-2.290	4.912	2.399
Br-BABA'-CN	-5.039	-2.297	4.797	2.405
Br-BBAA'-CN	-5.066	-2.307	4.773	2.407
Br-AABB'-CN	-5.011	-2.257	4.927	2.372
Br-ABBA'-CN	-5.086	-2.248	4.638	2.360
Br-AABBB'-CN	-4.899	-2.205	4.636	2.303
Br-BABAB'-CN	-4.946	-2.250	4.692	2.348
Br-BBAAA'-CN	-4.879	-2.312	4.801	2.397
Br-AABBBA'-CN	-4.860	-2.257	4.449	2.419
Br-BABABA'-CN	-4.875	-2.276	4.628	2.366
Br-BBAAAB'-CN	-4.889	-2.293	4.670	2.468

Compound	ZINDO (eV)	Osc. Str. (au)	TDDFT (eV)	Osc. Str (au)
Br-AA'-CN	3.971	1.600	3.482	1.463
Br-BA'-CN	3.756	0.963	3.064	0.949
Br-AB'-CN	3.793	1.080	3.187	0.855
Br-BB'-CN	3.736	0.857	2.982	0.990
Br-AAB'-CN	3.450	2.205	2.818	2.150
Br-BAA'-CN	3.381	1.995	2.816	1.722
Br-BAB'-CN	3.398	2.067	2.649	1.977
Br-ABA'-CN	3.500	2.317	2.615	1.961
Br-ABB'-CN	3.427	2.266	2.780	1.874
Br-BBA'-CN	3.438	2.154	2.679	1.925
Br-BAAB'-CN	3.218	2.778	2.539	2.593
Br-ABAB'-CN	3.234	2.920	2.376	2.517
Br-BABA'-CN	3.247	2.835	2.408	2.457
Br-BBAA'-CN	3.309	3.046	2.598	2.810
Br-AABB'-CN	3.264	2.913	2.416	2.436
Br-ABBA'-CN	3.300	3.001	2.508	2.598
Br-AABBB'-CN	3.544	2.575	2.338	3.420
Br-BABAB'-CN	3.746	2.715	2.356	3.265
Br-BBAAA'-CN	3.707	2.393	2.257	2.597
Br-AABBBA'-CN	3.502	3.032	2.202	3.813
Br-BABABA'-CN	3.655	3.531	2.256	3.928
Br-BBAAAB'-CN	3.778	3.063	2.237	3.560

Table S6. Computed ZINDO and TDDFT Excitation Energies and Oscillator Strengths

All ZINDO calculations were performed using the gas-phase PM6 geometry, while TDDFT calculations were performed as noted in the manuscript (B3LYP/6-31G*/CHCl₃).

Table S7. Computed DFT HOMO and LUMO Energies and ZINDO Excitations for All

Hexamer Sequences Containing Three A and Three B units

Compound	НОМО	LUMO	Gap	ZINDO (eV)	Osc. Str.
Br-AAABBB'-CN	-4.892	-2.266	2.626	3.583	2.862
Br-AABABB'-CN	-4.836	-2.261	2.575	3.628	3.406
Br-AABBAB'-CN	-4.927	-2.290	2.637	3.600	3.070
Br-AABBBA'-CN	-4.818	-2.267	2.551	3.502	3.032
Br-ABAABB'-CN	-4.873	-2.272	2.601	3.707	3.479
Br-ABABAB'-CN	-4.834	-2.277	2.557	3.695	3.552
Br-ABABBA'-CN	-4.904	-2.287	2.616	3.562	3.291
Br-ABBAAB'-CN	-4.952	-2.312	2.641	3.652	2.715
Br-ABBABA'-CN	-4.937	-2.332	2.605	3.594	3.440
Br-ABBBAA'-CN	-4.868	-2.312	2.556	3.517	3.021
Br-BAAABB'-CN	-4.951	-2.291	2.659	3.727	2.811
Br-BAABAB'-CN	-4.876	-2.285	2.591	3.729	3.353
Br-BAABBA'-CN	-4.896	-2.288	2.608	3.603	2.875
Br-BABAAB'-CN	-4.938	-2.311	2.627	3.782	3.296
Br-BABABA'-CN	-4.903	-2.298	2.605	3.655	3.531
Br-BABBAA'-CN	-4.933	-2.330	2.604	3.593	3.111
Br-BBAAAB'-CN	-4.874	-2.309	2.565	3.778	3.063
Br-BBAABA'-CN	-4.865	-2.299	2.565	3.720	3.706
Br-BBABAA'-CN	-4.964	-2.340	2.624	3.683	3.526
Br-BBBAAA'-CN	-4.956	-2.351	2.605	3.604	2.846

All calculations were performed as geometry optimizations upon the lowest-energy MMFF94 conformer using B3LYP/6-31G(d). ZINDO calculations were performed using the B3LYP optimized geometry.

Figure S68. Correlation Between DFT HOMO, Δ SCF(+) and Experimental Electrochemical Oxidation Potentials



Best Fit Multivariate Linear Regression:

-2.8076-0.3.88732*B3LYP/6-31G*/THF+0.328008*ΔSCF(+)

(Mean Unsigned Error: 0.041 eV)



Figure S69. Correlation Between DFT LUMO, ΔSCF(-) and Experimental Electrochemical Reduction Potentials



Best Fit Multivariate Linear Regression:

-2.40139-0.40082 *B3LYP/6-31G*/THF-0.194351*ΔSCF(-)

(Mean Unsigned Error: 0.036 eV)





Energies



Best Fit Multivariate Linear Regression:

-0.0506+0.5495*ZINDO(gas)+0.3298*TDDFT(solvent)

(Mean Unsigned Error: 0.071 eV)



Figure S71. Correlation Between Predicted ZINDO, TDDFT, and Consensus Oscillator Strengths vs. Experimental Optical Absorption Extinction Coefficients



Best Fit Multivariate Linear Regression:

-1024.80111+10605.2006733837*TDDFT+ 20155.49643*ZINDO

(Mean Unsigned Error: 6.7%)







REFERENCES

1. Norris, B. N.; Pan, T.; Meyer, T. Y., "Iterative synthesis of heterotelechelic oligo(phenylene-vinylene)s by olefin cross-metathesis" *Org. Lett.* **2010**, *12* (23), 5514-5517.

2. Miyakoshi, R.; Shimono, K.; Yokoyama, A.; Yokozawa, T., "Catalyst-Transfer Polycondensation for the Synthesis of Poly(p-phenylene) with Controlled Molecular Weight and Low Polydispersity" *J. Am. Chem. Soc.* **2006**, *128* (50), 16012-16013.

3. Li, Y.; Li, H.; Xu, B.; Li, Z.; Chen, F.; Feng, D.; Zhang, J.; Tian, W., "Molecular structure-property engineering for photovoltaic applications: Fluorene-acceptor alternating conjugated copolymers with varied bridged moieties" *Polymer* **2010**, *51* (8), 1786-1795.

4. Peng, Z.; Gharavi, A. R.; Yu, L., "Synthesis and characterization of photorefractive polymers containing transition metal complexes as photosensitizer" *J. Am. Chem. Soc.* **1997**, *119* (20), 4622-4632.

5. Olah, G. A.; Keumi, T., "Synthetic methods and reactions. 60. Improved one-step conversion of aldehydes into nitriles with hydroxylamine in formic acid solution" *Synthesis* **1979**, (2), 112-13.

6. Brandt, P.; Norrby, P.-O.; Martin, I.; Rein, T., "A Quantum Chemical Exploration of the Horner-Wadsworth-Emmons Reaction" *J. Org. Chem.* **1998**, *63* (4), 1280-1289.

 Markiewicz, J. T.; Schauer, D. J.; Lofstedt, J.; Corden, S. J.; Wiest, O.; Helquist, P., "Synthesis of 4-Methyldienoates Using a Vinylogous Horner-Wadsworth-Emmons Reagent. Application to the Synthesis of Trichostatic Acid" *J. Org. Chem.* 2010, 75 (6), 2061-2064.
 Bovicelli, P.; Borioni, G.; Fabbrini, D.; Barontini, M., "New efficient synthesis of

8. Bovicelli, P.; Borioni, G.; Fabbrini, D.; Barontini, M., "New efficient synthesis ubiquinones" *Synth. Commun.* **2008**, *38* (3), 391-400.

9. Yang, J.-S.; Hwang, C.-Y.; Hsieh, C.-C.; Chiou, S.-Y., "Spectroscopic correlations between supermolecules and molecules. Anatomy of the ion-modulated electronic properties of the nitrogen donor in monoazacrown-derived intrinsic fluoroionophores" *J. Org. Chem.* **2004**, *69* (3), 719-726.

10. Li, Z.; Badaeva, E.; Zhou, D.; Bjorgaard, J.; Glusac, K. D.; Killina, S.; Sun, W., "Tuning Photophysics and Nonlinear Absorption of Bipyridyl Platinum(II) Bisstilbenylacetylide Complexes by Auxiliary Substituents" *J. Phys. Chem. A* **2012**, *116* (20), 4878-4889.

11. Albers, H. M. H. G.; Hendrickx, L. J. D.; van Tol, R. J. P.; Hausmann, J.; Perrakis, A.; Ovaa, H., "Structure-Based Design of Novel Boronic Acid-Based Inhibitors of Autotaxin" *J. Med. Chem.* **2011**, *54* (13), 4619-4626.

Full text of Reference 70:

Gaussian 09. Revision A.02. Frisch. M. J.: Trucks. G. W.: Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.