Molecular engineering of nanoscale order in organic electro-optic glasses†

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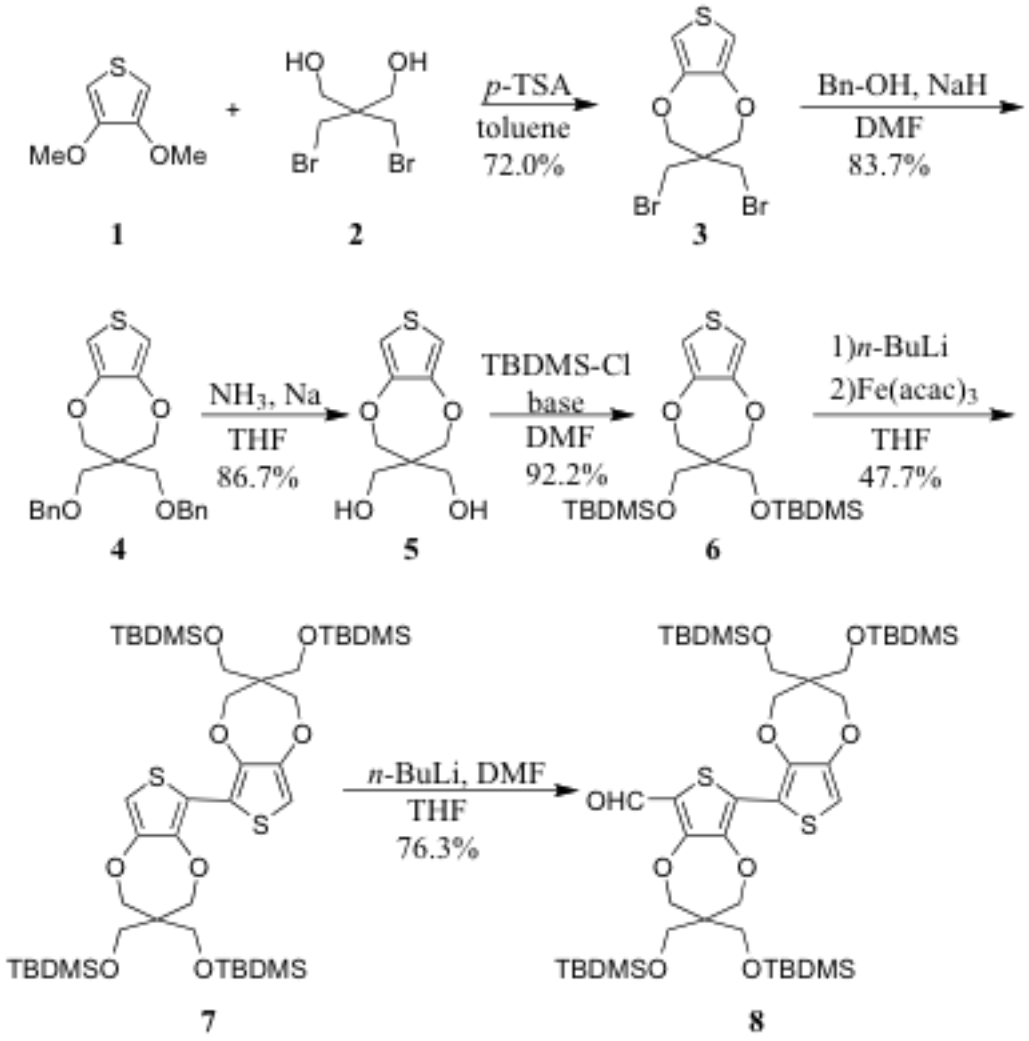
Electronic Supporting Information

Synthesis

The synthesis of **OLD-5** is presented in Schemes S1 and S2. To synthesize the bridge (Scheme 1), 3,4-dimethoxythiophene (**1**) was coupled to 2,2-bis(bromomethyl)-1,3-propanediol (**2**) in a transetherification reaction to give the dibromo ProDOT moiety (**3**) in 72.0% yield.[1] This was then converted to the benzyl protected dihydroxy ProDOT (**4**) via a Williamson etherification in 83.7% yield. This route was required as the ProDOT ring formation reaction can be disrupted by the presence of extraneous alkoxy moieties in the molecules, and the use of pentaerythritol [$C(CH_2OH)_4$] leads to the undesirable formation of two connected ProDOT rings.[2] The benzyl group was then removed using a Birch reduction (**5**, 86.7%) and replaced with a TBDMS group (**6**, 92.2%), which allows for facile deprotection of the final chromophore. The TBDMS-protected ProDOT (**6**) was dimerized with *n*-BuLi, tetraethylenediamine (TMEDA), and $Fe(acac)_3$ to give **7** in 47.7% yield. The dimer (**7**) was then selectively mono-formylated using 1 equivalent of *n*-BuLi with DMF to give **8** in 76.3% yield.

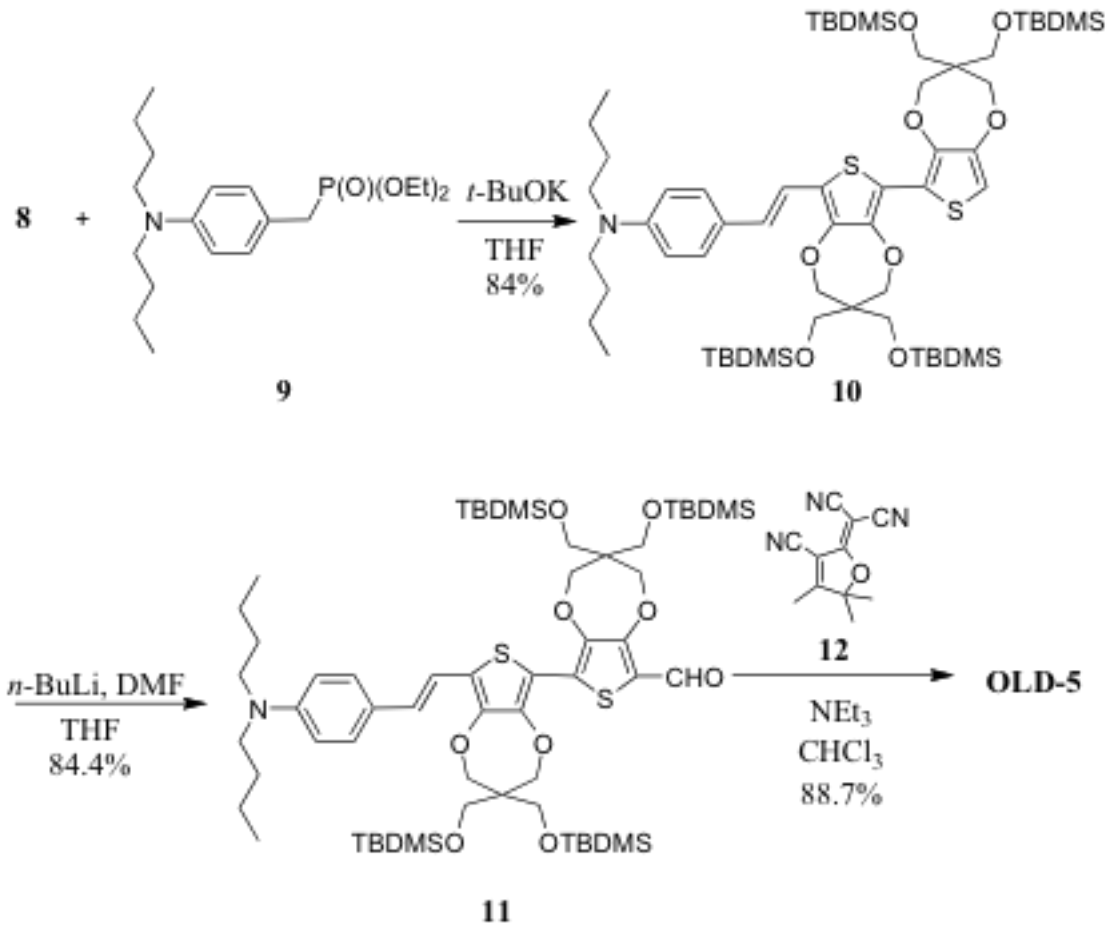
Scheme S1. Synthesis of ProDOT(CH_2OTBDMS)$_2$-based bridge



The donor (**9**) was attached to the bridge-aldehyde (**8**) (Scheme 2) using a Horner-Wadsworth-Emmons reaction to give the donor-bridge (**10**) in 84.0% yield. The donor-bridge (**10**) was then formylated using *n*-BuLi and DMF to give **11** in 84.4% yield. Finally, the tricyanofuran-based acceptor (TCF, **12**)[3, 4] was attached using a Knoevenagel condensation to afford **OLD-5** in 88.7% yield. In theory, **OLD-5** itself could be explored as an EO chromophore in guest-host films. To our surprise, however, it did not prove to be sufficiently soluble. Although **OLD-5** is moderately soluble in common

organic solvents, it does not display the high degree of solubility necessary for spin casting high-quality EO films. It can, however, be further derivatized into high-molecular weight dendronized chromophores with aspect ratios near 1.5.

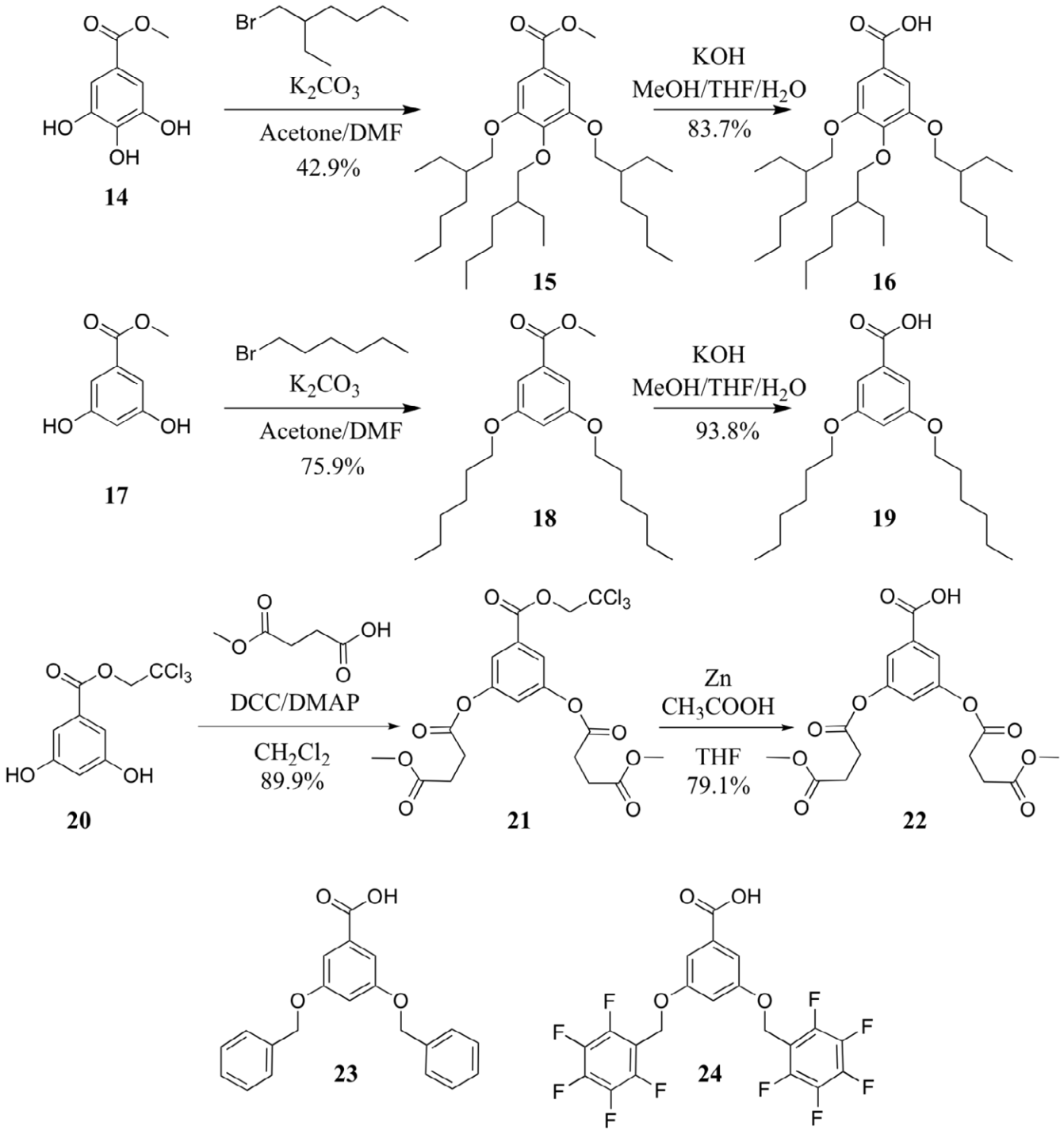
Scheme S2. Synthesis of **OLD-5** chromophore



The synthesis of the dendrons is presented in Scheme S3. The commercially available methyl 3,4,5-trihydroxybenzoate (**14**) was alkylated with 1-bromo-2-ethylhexane to afford the tris-2-ethylhexyl derivative (**15**) in 42.9 % yield. This was then deprotected with potassium hydroxide (KOH) in methanol (MeOH), tetrahydrofuran (THF), and water to afford the carboxylic acid (**16**) in 83.7 % yield. The second dendron was synthesized by alkylating the commercially available methyl 3,5-dihydroxybenzoate (**17**) with 1-bromohexane to afford the dihexyl derivative (**18**) in 75.9 % yield. This was then deprotected using KOH in MeOH/THF/water to afford the acid (**19**) in 93.8 % yield. The third dendron was synthesized by esterification of the commercially available 2,2,2-trichloroethyl 3,5-

dihydroxybenzoate (**20**) with monomethyl succinate to afford the bis-diester derivative (**21**) in 89.9 % yield. This was then selectively deprotected with zinc dust in acetic acid and THF to afford the carboxylic acid derivative (**22**) in 79.1 % yield. The fourth dendron used was the commercially available 3,5-dibenzyloxybenzoic acid (**23**). The fifth and final dendron studied was synthesized via the literature method to afford the acid (**24**).[5]

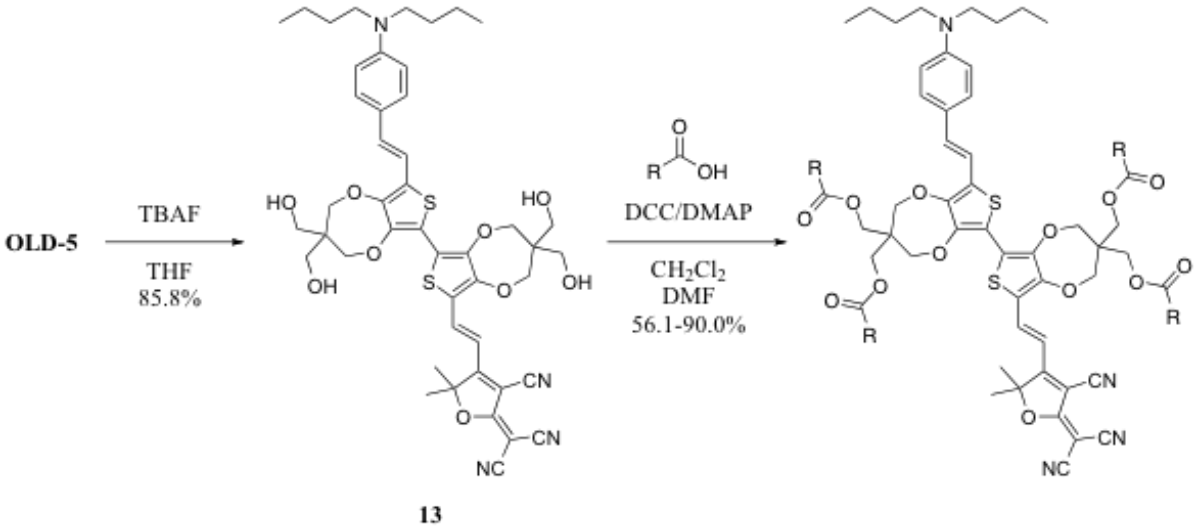
Scheme S3. Synthesis of dendrons for pseudo-discotic chromophores



As the ProDOT ring is highly acid sensitive, **OLD-5** must be deprotected under mildly basic tetrabutylammounium fluoride (TBAF) conditions (Scheme S3), which affords the tetra-alcohol derivative (**13**) in 85.8 % yield. The tetra-ol product (**13**) can then be esterified under dicyclohexylcarbodimide (DCC) and dimethylaminopyridine (DMAP) conditions with a variety of

carboxylic acid containing dendrons to afford the pseudo-discotic chromophores. The yields for this reaction varied widely from 56.1% (**SJLD-3**) to 90.0 % (**SJLD-2**), depending on the dendron structure.

Scheme S4. Generic synthesis of pseudo-discotic chromophores



Film Properties

Figure S1 displays optical microscopy of the crystalline platelets that form in cured films of **SJLD-1**. Note that these crystals are a different polymorph from the crystals of **SJLD-1** obtained from binary solvent diffusion experiments, and are also distinct from the crystal forms seen in **SJLD-4** and **-5.**

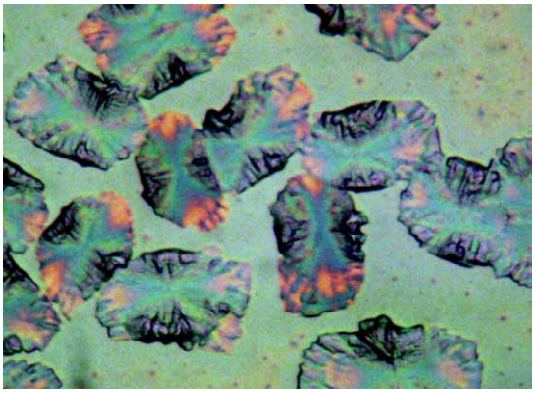


Figure S1. Crystallites of **SJLD-1** in cured films (bright field optical microscopy, 100x)

Aged (>6 months) amorphous films of **SJLD-2**, stored in the dark at room temperature (above the T_g), show distinct microscopic dendritic patterns under optical microscopy (Figure S2). These features

likely arise from spontaneously self-assembled regions that slowly develop, as the material is mobile above its T_g.

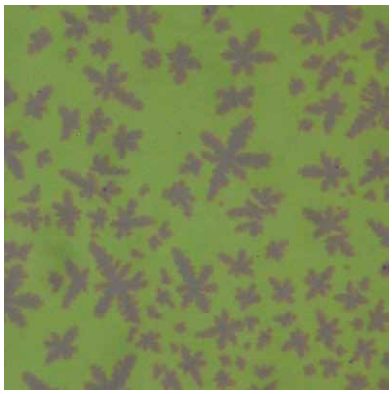


Figure S2. Dendritic patterns in aged amorphous **SJLD-2** films (bright field optical microscopy, 500x)

We have examined the surface morphology of freshly prepared cured self-assembled (SA) and amorphous films of **SJLD-2** via atomic force microscopy (AFM) in contact mode. The amorphous films (Figure S3, left) are inherently relatively smooth with a 0.72 nm root-mean-squared surface roughness (R_q, restricted area), but also exhibit distinct phases within the amorphous material, visible as small dendritic regions in the AFM image. In contrast, the SA films (Figure S3, right) exhibit a uniform striped texture, and a significantly larger R_q of 9.5 nm. This may be due to the self-assembly process, or may be a consequence of surface deformation from the AFM tip, as the sample is above its T_g.

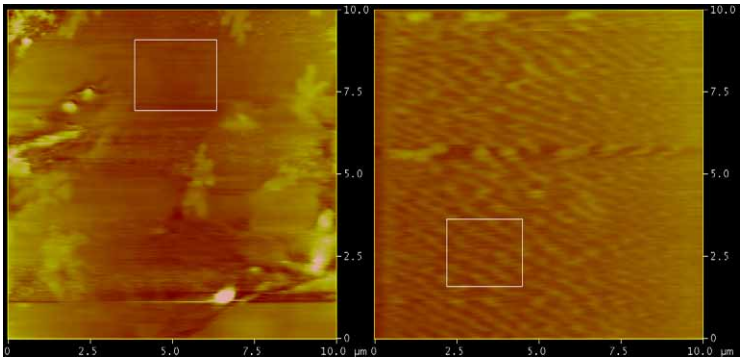


Figure S3. AFM images of amorphous (left) and self-assembled (right) films of **SJLD-2**

We have also examined the surface morphology of freshly prepared cured SA and amorphous films of **SJLD-4** via AFM in contact mode. The amorphous films (Figure S4, left) are very smooth, albeit with some surface features, with a R_q of 0.68 nm. There is no sign of dendritic growths, in accordance with

the relatively high T_g of **SJLD-4**. In contrast, the SA films (Figure S4, right) are significantly rougher, with a R_q of 2.6 nm.

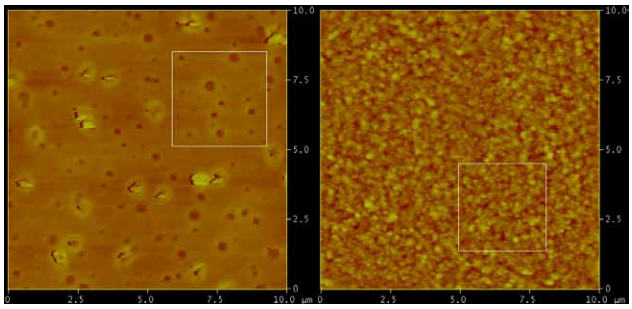


Figure S4. AFM images of amorphous (left) and self-assembled (right) films of **SJLD-4**

Presented in Figure S5 is the small-angle XRD spectrum of a representative mixed polycrystalline/amorphous film of **SJLD-3** (cast from TCE), which may be compared to those of the SA films of **SJLD-2** and **SJLD-4**. Although the peaks are in a ratio of 1:3:4:5, which is consistent with the order in the SA films, the peaks are significantly sharper, indicating a higher degree of order, and the relative intensities of the peaks is different than in the SA films, with the third order peak being of highest intensity. All attempts to date to grow single-crystals of **SJLD-3** from solution have failed.

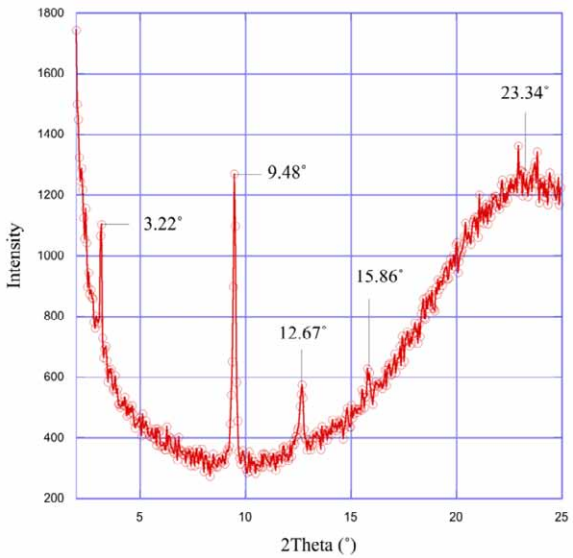


Figure S5. XRD spectrum of representative **SJLD-3** polycrystalline/amorphous film

Thermal Properties

The DSC traces of as-prepared bulk **SJLD-1** are provided in Figure S6. The sharply negative baseline for the trace on the right is due to an instrumental calibration issue. The DSC trace of as-prepared bulk **SJLD-2** is presented in Figure S7. The DSC trace of as-prepared bulk **SJLD-3** is presented in Figure S8, with an expansion of the region surrounding the T_g on the right. DSC trace of as-prepared bulk **SJLD-5** is presented in Figure S9.

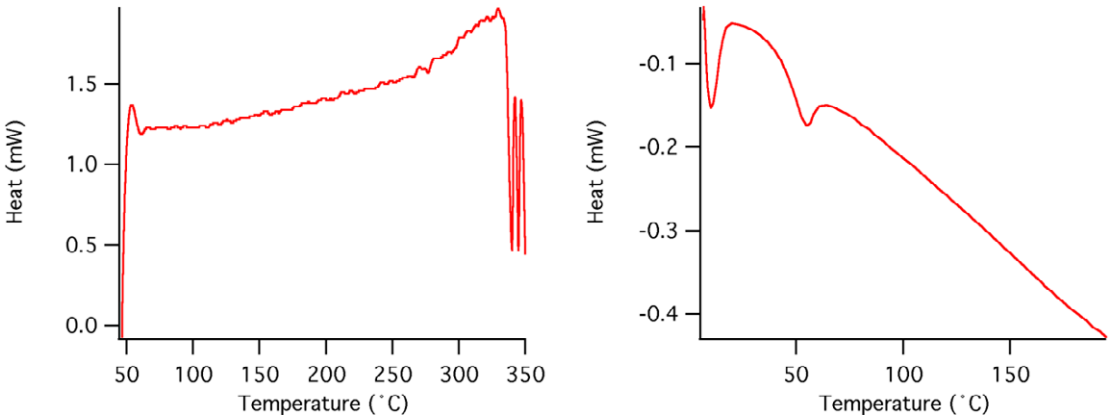


Figure S6. DSC traces of bulk **SJLD-1**, 10 ˚C/min, N_2 atmosphere

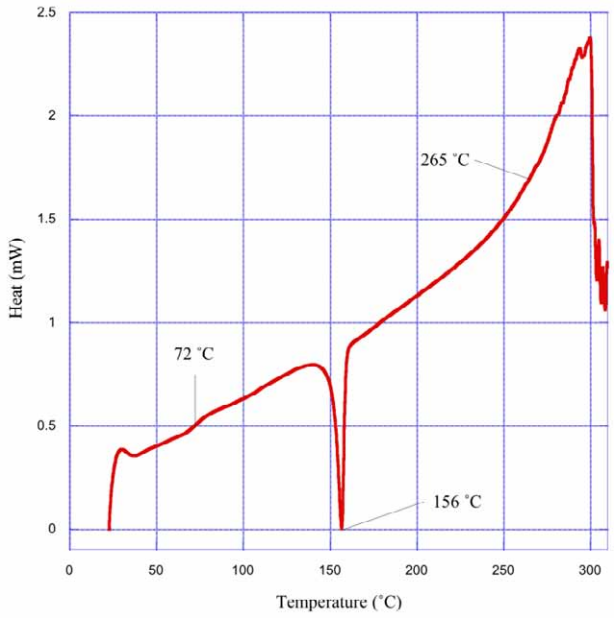


Figure S7. DSC trace of bulk **SJLD-2**, 10 ˚C/min, N_2 atmosphere

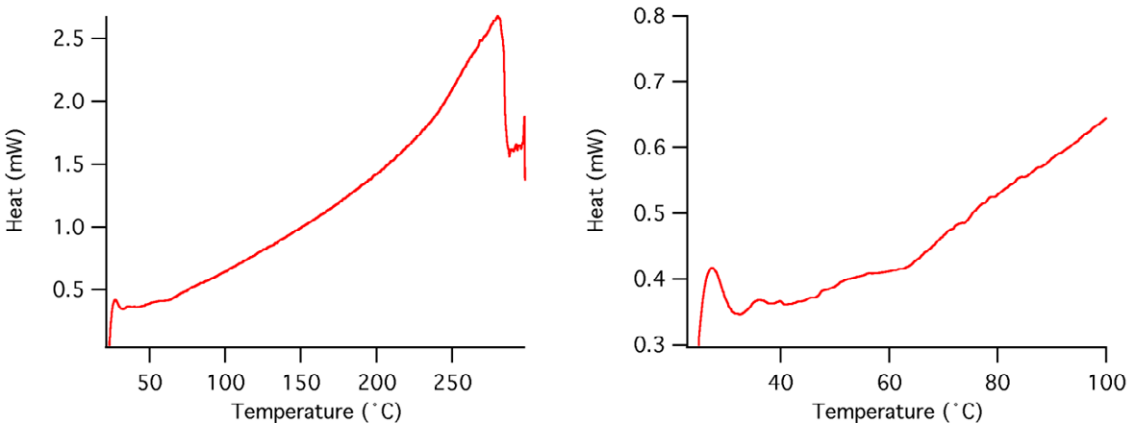


Figure S8. DSC trace of bulk **SJLD-3**, 10 ˚C/min, N_2 atmosphere, with expansion of T_g region (right)

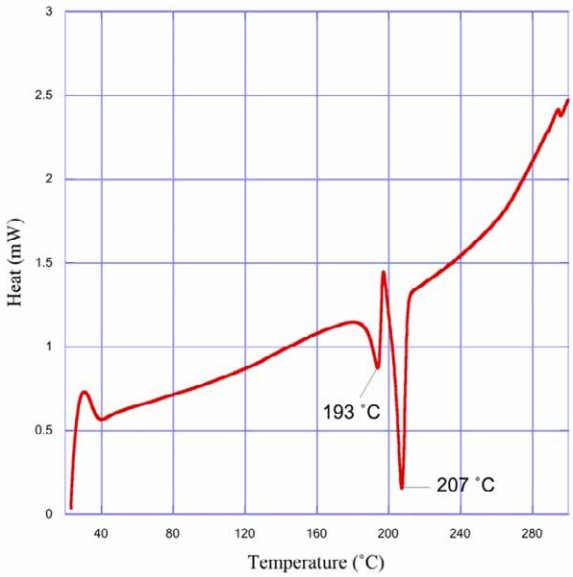


Figure S9. DSC trace of bulk **SJLD-5**, 10 ˚C/min, N_2 atmosphere

Presented in Figure S10 are bright field (left) and cross polarizer (right) optical microscopy images of crystallized **SJLD-4**, seen in the VTM experiments. Note that the dichroism of the crystals under polarized illumination indicates that the transition dipole moment of the chromophore (molecular long axis) is perpendicular to the long axis of the crystals. The green color of the crystals suggests a very different molecular conformation than in the SA films or in the crystals of **SJLD-1**. We have so far been unsuccessful in our attempts to grow single-crystals of **SJLD-4**, which could provide important structural information of this different polymorph.

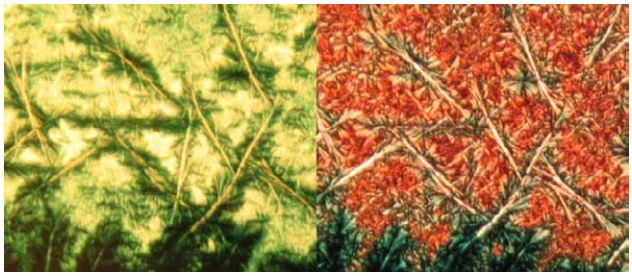


Figure S10. Optical microscopy images of **SJLD-4** crystals under bright field (left) and crossed polarizer (right) illumination (100x)

Crystallography

The XRD structure of **SJLD-1** is shown in Figure S11. Although the structure is not fully resolved, with the 2-ethylhexyl dendron side-chains incompletely resolved, the structure correctly identifies the key elements of the molecular structure including the charge-transfer backbone, the ProDOT rings, and the dendron core structures. The inability to fully resolve the side-chains is likely due to inherent disorder in their conformations within the crystal, which is evident in the increased size of the disorder ellipsoids in the ORTEP view of the structure (Figure S12). As such, we feel confident that the structure accurately represents the important details of the crystals, including the key intermolecular interactions.

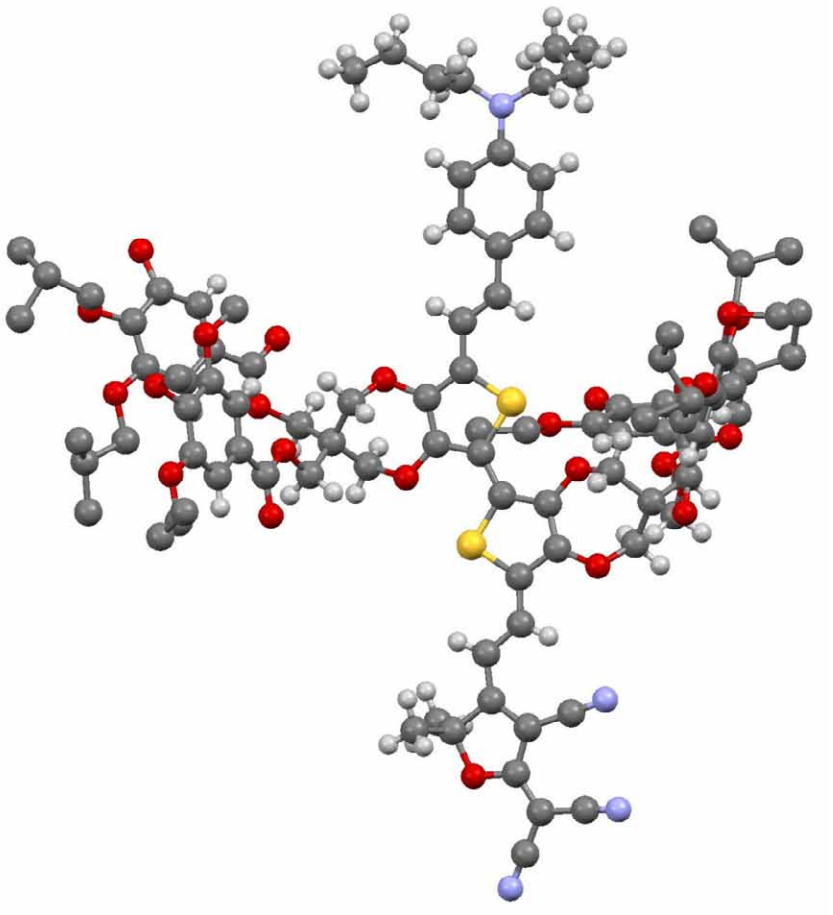


Figure S11. Synchrotron X-ray structure of **SJLD-1**

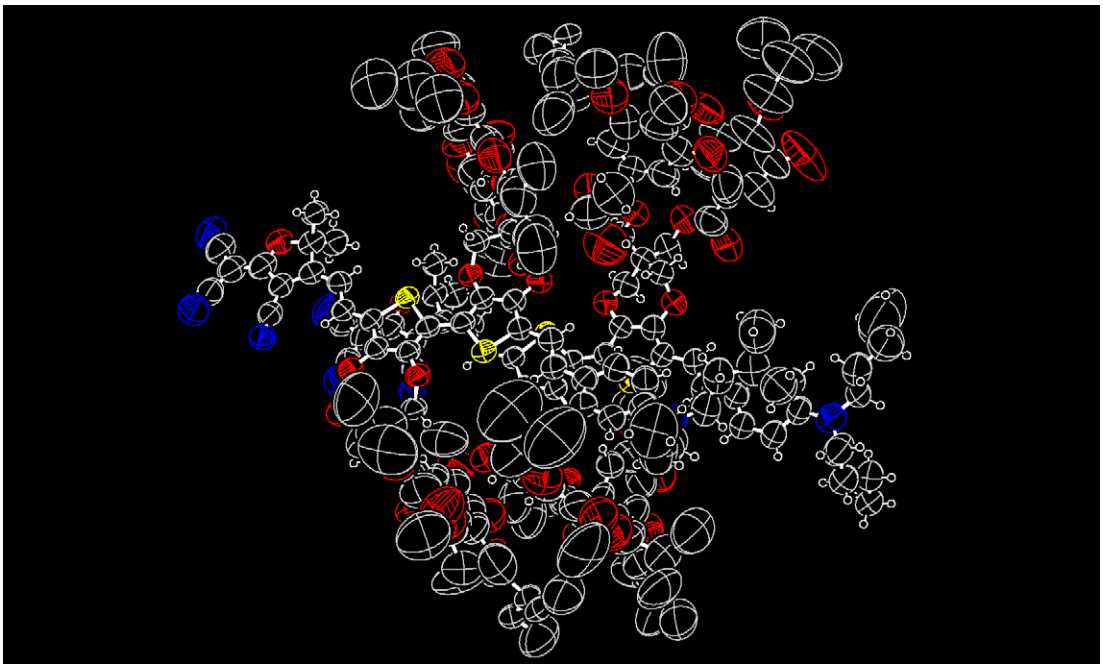


Figure S12. ORTEP view of synchrotron X-ray structure of **SJLD-1**

The extended cell obtained by tiling out the unit cell, presented in Figure S13, provides further information about the weak intermolecular interactions in the **SJLD-1** crystal that give rise to its extremely touch sensitive nature. Interestingly, the strong π-π stacking interactions between chromophore conjugated backbones appears to be limited to within the unit cell, as there are minimal interactions between chromophore backbones along the crystallographic a axis. Along both the crystallographic a and b axes the only interactions between unit cells appears to be relatively weak Van der Waals interactions between dendron alkyl chains and incorporated solvents. The relatively weak interactions here likely contribute to the extremely touch sensitive nature of these crystals.

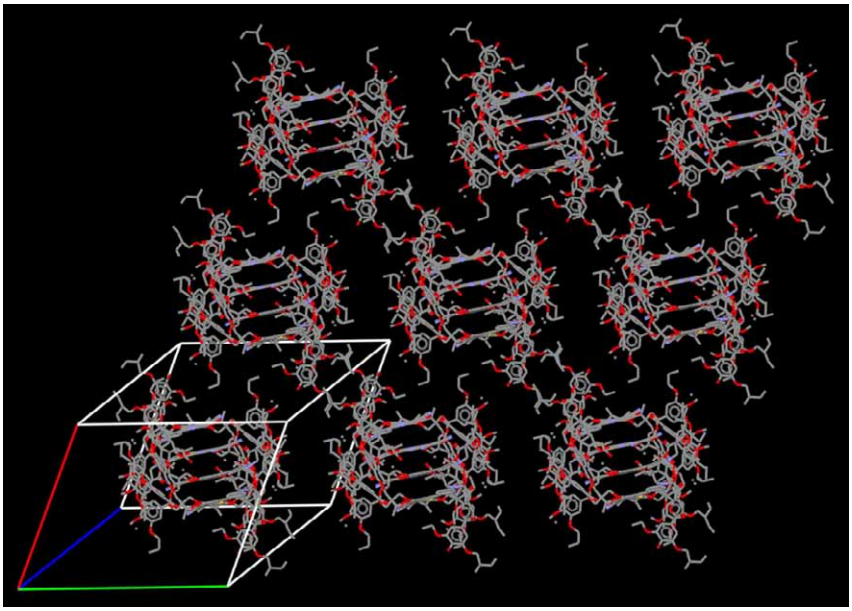


Figure S13. 3 by 3 by 1 cell crystal structure of **SJLD-1**

Experimental

General

All commercially available starting materials were purchased from Sigma-Aldrich, ACROS, or TCI and used without further purification unless otherwise stated. HPLC grade tetrahydrofuran (THF), diethyl ether, methylene chloride, and toluene were purchased from Fisher chemical and purified by passing through alumina in a Seca Solvent Systems (GlassContour Systems) solvent purification system. Alkyl lithium reagents were purchased from ACROS and titrated using 4-biphenylmethanol according to the literature method.[6] All reactions were performed under a nitrogen or argon atmosphere

unless otherwise stated. Flash chromatography was performed manually using fine mesh silica. 3,4-dimethoxythiophene,[7] 2-dicyanomethylen-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (TCF),[3] and 3,5-bis(perfluorobenzyloxy)benzoic acid[5] were synthesized as reported in literature.

Instrumentation

Atomic force microscopy was performed on a Digital Multimode AFM in the Nanotechnology User Facility (Center for Nanotechnology, University of Washington). ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AV300 or AV301 system at 300Mhz and referenced to residual solvent. Mass spectrum data was obtained from positive ion ESI or MALDI at the Medicinal Chemistry Mass Spectrometry facilities at the University of Washington. Elemental analyses were performed at Prevalere Life Science Inc. (Whitesboro, New York).

Synthesis of OLD-5 Chromophore

3,3-Bis(bromomethyl)-2,4-dihydro-2H-theino[3,4-b][1,4]-dioxepine [ProDOT($CH_2Br)_2$] (3).[1] 3,4-methoxythiophene (**1**, 10.00 g, 69.4 mmol), *p*-toluenesulfonic acid (1.53 g, 8.90 mmol), and 2,2-Bis(bromomethyl)-1,3-propanediol (**2**, 32.69 g, 124.8 mmol) were dissolved in 200 mL toluene. The reaction flask was equipped with a Soxhlet extractor containing 4A molecular sieves and the reaction was heated to reflux and allowed to stir overnight. The mixture was then cooled to room temperature and placed in the freezer. The precipitate was filtered out and rinsed with cold toluene. The organic layers were combined and the solvent removed under reduced pressure. The crude compound was purified with a silica plug using 1:1 hexane, dichloromethane to give 17.08 (72.0%) pure product. ^{1}H NMR ($CDCl_3$): δ 6.50(s, 2H), 4.10(s, 4H), 3.61(s, 4H).

3,3-Bis(benzyloxymethyl)-3,4-dihydro-2H-thieno-[3,4-b][1,4]dioxepine [ProDOT($CH_2OBn)_2$] (4).[1] A dry 250 mL flask was filled with 150 mL of DMF and benzyl alcohol (5.5 mL, 53.1 mmol) and NaH (2.15 g, 53.8 mmol). The solution was heated to 110 °C and stirred overnight. ProDOT($CH_2Br)_2$ (**3**) (6.05 g, 17.7 mmol) was added and the reaction was heated for another 4 hours at which point another equivalent of NaH (0.71 g, 17.7mmol) was again added. The solution was stirred overnight at 110 °C. Upon completion, the reaction was cooled to room temperature and poured into 400 mL of

brine and extracted three times with ether. The combined organic layers were washed three times with water, dried with Na_2SO_4 and the solvent was removed under reduced pressure. The resulting orange oil was purified by silica column chromatography (1:1 hexane, dichloromethane) to give a white solid (5.82 g, 83.0%). ^{1}H NMR ($CDCl_3$): δ 7.31 (m, 10H), 6.45(s, 2H), 4.51(s, 4H), 4.07(s, 4H), 3.62(s, 4H). ^{13}C NMR ($CDCl_3$): δ 149.53, 138.24, 128.28, 127.50, 127.36, 105.07, 73.52, 69.26, 47.74. ES+ MS 397.0 (M+H). Elem. Anal.: Calc.: C 69.97, H 6.10 %. Found: C 69.39, H 6.05 %

3,3-Bis(hydroxymethyl)-3,4-dihydro-2H-thieno-[3,4-b][1,4]dioxepine [ProDOT(CH_2OH)$_2$] (5). Ammonia (250 mL) was condensed into a dry 500 mL flask at -78 °C and sodium metal (1.20 g, 52.0 mmol) was added. ProDOT(CH_2OBn)$_2$ (**4**) (4.97 g, 12.5 mmol) was dissolved in 10 mL of THF and added dropwise to the NH_3/Na mixture. The reaction was stirred for 15 minutes at -78 °C and was then quenched with solid NH_4Cl. The ammonia was evaporated off and the resulting solid was dissolved in water and extracted two times with ether. The combined organic layers were dried with Na_2SO_4 and the solvent was removed under reduced pressure to give the crude product. The crude product was recrystallized in ethyl acetate to give a white solid (2.34 g, 86.7%). ^{1}H NMR (DMSO): δ 6.69(s, 2H), 4.32(t, J = 5.1 Hz, 2H), 3.88(s, 4H), 3.45(d, J = 5.4 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ 149.44, 105.27, 72.91, 59.63, 47.88. ES+ MS 216.9 (M+H). Elem. Anal.: Calc.: C 49.99, H 5.59 %. Found: C 50.47, H 5.90 %

3,3-Bis(*t*butyldimethylsilylmethylether)-3,4-dihydro-2H-thieno-[3,4-b][1,4]dioxepine [ProDOT($CH_2OTBDMS$)$_2$] (6). Diisopropylethyl amine (0.84 mL, 4.82 mmol) was added to a solution of ProDOT(CH_2OH)$_2$ (**6**) (0.413 g, 1.91 mmol) and dry DMF (10 mL). Chloro-*t*-butyl-dimethylsilane (0.72 g, 4.79 mmol) was added to the mixture in portions. The reaction was stirred at room temperature for 24 hours, poured into water and extracted with ethyl acetate. The combined organic layers were dried with Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was then purified by silica column chromatography using 9:1 hexane, ethyl acetate to yield the pure product (0.740 g, 87.1%). ^{1}H NMR ($CDCl_3$): δ 6.40(s, 2H), 3.94(s, 4H), 3.65(s, 4H), 0.87(s, 18H),

0.03(s, 12H).). ^{13}C NMR ($CDCl_3$): δ 149.54, 104.66, 73.12, 61.22, 48.79, 25.81, 18.19, -5.65. ES+ MS 445.1 (M+H). Elem. Anal.: Calc.: C 56.71, H 9.06 %. Found: C 57.00, H 9.14 %

2,2'-Bi{3,3-Bis(*t*butyldimethylsilylmethylether)-3,4-dihydro-2H-thieno-[3,4-b][1,4]dioxepine} Bi[ProDOT(CH_2OTBDMS)$_2$] (7). *n*-butyl lithium (6.7 mL, 1.66 M in hexane) was added dropwise to a solution of ProDOT(CH_2OTBDMS)$_2$ (**6**) (4.33 g, 9.74 mmol) and N,N,N,N-tetramethylethyldiamine (TMEDA) (3.2 mL, 21.4 mmol) in dry THF (30 mL) at -15 ºC. The solution was stirred for 45 min at -10 ºC and then transferred via canula to a mixture of $Fe(acac)_3$ (3.44 g, 9.74 mmol) in THF (40 mL) at reflux. The mixture was stirred overnight at reflux, cooled to room temperature and the solvent was removed under reduced pressure. The crude material was purified by column chromatography using 9:1 hexane, dichloromethane to give 2.06 g (47.7%) pure product. ^{1}H NMR ($CDCl_3$): δ 6.37(s, 2H), 4.07 (s, 4H), 4.00(s, 4H), 3.72(s, 8H), 0.92(s, 36H), 0.08(s, 24H). ^{13}C NMR ($CDCl_3$): δ 149.03, 144.72, 114.95, 102.52, 73.36, 73.18, 61.29, 48.87, 25.01, 18.19, -5.69. MALDI-MS 886.3. Elem. Anal.: Calc.: C 56.84, H 8.86 %. Found: C 56.92, H 9.31 %

2-{2,2'-Bi{3,3-Bis(*t*butyldimethylsilylmethylether)-3,4-dihydro-2H-thieno-[3,4-b][1,4]dioxepine}} carboxaldehyde (8). The bi(ProDOT(CH_2OTBDMS)$_2$) (**7**) (1.16 g, 1.31 mmol) was dissolved in 15 mL dry THF and cooled to -78 °C. *n*-BuLi (0.79 mL, 1.66 M in hexane) was added dropwise and the reaction was stirred at -78 °C for 60 minutes. DMF (0.15 mL, 1.97 mmol) was then added and the solution was allowed to warm slowly to room temperature. The reaction was quenched with brine and the product was extracted with ether. The combined organic layers were dried with Na_2SO_4 and the solvent was removed under reduced pressure. The monoformylated product was obtained through purification by silica column chromatography (3:7 dichloromethane, hexane) to give a yellow solid (0.961 g, 76.3%). ^{1}H NMR ($CDCl_3$): δ 9.92(s, 1H), 6.52 (s, 1H), 4.11(m, 8H), 3.72(s, 8H), 0.90(s, 36H), 0.07(s, 24H). ^{13}C NMR ($CDCl_3$): δ 180.94, 149.10, 147.50, 143.60, 73.72, 61.65, 61.42, 48.80, 48.76, 25.84, 18.23, -5.61. ES+ MS 915.4244 (M+H) Elem. Anal.: Calc.: C 56.41, H 8.59 %. Found: C 55.23, H 8.63 %

2-{2-[4-(*N,N*-Diethylamino)phenyl]vinyl}-[bi(ProDOT(CH$_2$OTBDMS)$_2$)] (10). The amino phosophonate (**9**) (0.49 g, 1.37 mmol) and bridge (**8**) (1.10 g, 1.20 mmol) were dissolved in 10 mL of dry THF. The solution was cooled in a cold water bath and *t*-BuOK (1.5 mL, 1.0 M in THF) was added dropwise. The solution was stirred for 3 hours and poured into sat. $NaHCO_3$. The product was extracted with ether and the combined organic layers were dried using Na_2SO_4. The solvent was removed under reduced pressure. The crude product was purified by silica column chromatography (7:3 hexane, dichloromethane) to give a yellow solid (1.13 g, 84.0%). ^{1}H NMR ($CDCl_3$): δ 7.32(d, 8.7 Hz, 2H), 6.99(d, 16.2 Hz, 1H), 6.73(d, 16.2 Hz, 1H), 6.60(d, 8.6 Hz, 2H), 6.34(s, 1H), 4.05 (m, 8H), 3.76(m, 8H), 3.28(m, 4H), 1.56(m, 4H), 1.35(m, 4H), 0.92(m, 42H), 0.09(s, 24H). ^{13}C NMR ($CDCl_3$): δ 149.06, 147.42, 145.11, 144.95, 144.50, 127.35, 125.87, 124.67, 120.382, 115.20, 113.58, 111.57, 111.15, 102.43, 73.57, 73.30, 73.07, 61.38, 50.71, 48.85, 29.44, 25.82, 20.28, 18.22, 18.19, 13.95, -5.59. MALDI-MS 1115.3. Elem. Anal.: Calc.: C 62.37, H 9.11, N 1.25%. Found: C 62.30, H 9.01, N 1.38 %

5-{2-[4-(*N,N*-Diethylamino)phenyl]vinyl}-[bi(ProDOT(CH$_2$OTBDMS)$_2$)]-5'-carboxaldehyde (11). Compound **10** (1.36 g, 1.22 mmol) was dissolved in 30 mL dry THF and cooled to -78 °C. *n*-BuLi (1.35mL, 1.47 M in hexane) was added dropwise and the solution was stirred at -78 °C for 60 minutes. The bath was removed and the solution was allowed to warm for 5 minutes, at which point DMF (0.20 mL, 2.44 mmol) was added to the reaction. The solution was then warmed to room temperature and the reaction was quenched with brine. The product was extracted with ether, the combined organic layers were dried with Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified using silica column chromatography (7:3 hexane, dichloromethane ramped to 3:2) to give a red solid (1.18 g, 84.4%). ^{1}H NMR ($CDCl_3$): δ 9.89(s, 1H), 7.34(d, 9.0 Hz, 2H), 6.97(d, 16.5 Hz, 1H), 6.81(d, 16.0 Hz, 1H), 6.60(d, 8.6 Hz, 2H), 4.16 (m, 8H), 3.75(m, 8H), 3.28(m, 4H), 1.58(m, 4H), 1.38(m, 4H), 0.92(m, 42H), 0.09(s, 24H). ^{13}C NMR ($CDCl_3$): δ 180.61, 155.69, 148.02, 147.94, 145.09, 143.27, 127.91, 127.79, 126.50, 124.56, 124.29, 117.93, 113.19,

111.67, 74.05, 73.94, 73.69, 61.82, 61.63, 50.81, 48.84, 29.55, 25.92, 20.38, 18.31, 14.04, -5.54. ES+ MS 1144.6071 (M+H). Elem. Anal.: Calc.: C 61.89, H 8.89, N 1.22%. Found: C 61.48, H 8.61, N 1.17 %

2-[3-Cyano-4-(2-{5-[2-(4-diethylaminophenyl)vinyl]-[bi(ProDOT(CH_2OTBDMS)$_2$)-yl]}-vinyl)-5,5-dimethyl-5H-furan-2-ylidene]-malononitrile (OLD-5). The donor-bridge-aldehyde (**11**) (0.40 g, 0.35 mmol) and TCF acceptor (**12**) (0.84 g, 0.42 mmol) were dissolved in 5 mL chloroform. The solution was heated to reflux in a vessel equipped with a soxhlet containing 4Å molecular sieves. Once the solution was refluxing, 0.1 mL triethylamine was added. The solution was refluxed overnight and then poured into sat. NaCl. The product was separated out and the water was washed with chloroform. The combined organic layers were dried with Na_2SO_4 and the solvent was removed under reduced pressure. The crude material was then purified by silica column chromatography (1:1 hexane, dichloromethane ramped to 7:3 dichloromethane, hexane) to give the pure product (0.43 g, 92.7%). ^{1}H NMR ($CDCl_3$): δ 7.73(d, J = 15.6 Hz, 1H), 7.35(d, 8.8 Hz, 2H), 7.00(d, 16.1 Hz, 1H), 6.86(d, 16.2 Hz, 1H), 6.60(d, 8.9 Hz, 2H), 6.45(d, 15.7 Hz, 1H), 4.16(m, 8H), 3.76(m, 8H), 3.30(m, 4H), 1.75(s, 6H), 1.58(m, 4H), 1.38(m, 4H), 0.93(m, 42H), 0.09(s, 24H). ES+ MS 1325.6757 (M+H). Elem. Anal.: Calc.: C 63.40, H 8.21, N 4.22%. Found: C 63.25, H 7.86, N 4.10 %

Synthesis of Dendrons

3,4,5-Tris-(2-ethyl-hexyloxy)-benzoic acid methyl ester (15). In a 250 mL flask, methyl 3,4,5-trihydroxybenzoate (**14**, 2.75 g, 11.3 mmol) and 2-ethylhexylbromide (6.75 mL, 33.2 mmol) were dissolved in a mixture of 15 mL acetone and 7 mL DMF. To this solution was added K_2CO_3 (14.67 g, 106.1 mmol). The reactants were stirred at reflux for 24 hours. The cooled solution was then poured into 200 mL water and extracted with dichloromethane. The organic layer was dried with Na_2SO_4 and the solvent was removed under reduced pressure. The resulting crude product was purified by silica column chromatography using 1:1 hexane, dichloromethane kept under vacuum at 30 °C for 3 days to give 2.53 g (42.9%) of pure product. ^{1}H NMR ($CDCl_3$): δ 6.40(s, 2H), 3.94(s, 4H), 3.65(s, 4H), 0.87(s, 18H), 0.03(s, 12H).

3,4,5-Tris-(2-ethyl-hexyloxy)-benzoic acid (16). The methyl ester **15** (2.52 g, 4.83 mmol) was dissolved in a mixture of 25 mL methanol and 25 mL THF. To this was added a solution of potassium hydroxide (0.445 g, 9.67 mmol) dissolved in 10 mL water and the reaction was stirred for 48 hours at room temperature. The solvent was then removed under reduced pressure and the resulting mixture was neutralized with 1 M HCl. The product was extracted using dichloromethane, washed twice with water and once with sat. NaCl. The organic layer was then dried with Na2SO4 and the solvent was removed under reduced pressure to give the pure product (2.05 g, 83.7 %). ^{1}H NMR (acetone-d_6): δ 7.32(s, 2H), 3.96(m, 6H), 1.3-1.8(m, 36H), 0.93(m, 18H).

Methyl 3,5-Bis-hexyloxy-benzoate (18). A mixture of methyl 3,5-dihydroxybenzoate (**17**, 2.500 g, 14.87 mmol), 1-bromohexane (20.8 mL, 149 mmol), K_2CO_3 (20.5 g, 149 mmol), and 5 drops of Aliquat 336 phase-transfer catalyst were brought to reflux with vigorous stirring. The reactants were stirred at reflux for 24 hours. The cooled solution was then filtered and washed 2 x 50 mL deionized water. The organic layer was dried with Na_2SO_4 and the solvent was removed under reduced pressure. The resulting crude product was purified by silica column chromatography using 9:1 hexanes : ethyl acetate to afford 3.797 g (75.9%) of pure product. ^{1}H NMR ($CDCl_3$): δ 7.15 ppm(d, 2.3 Hz, 2H), 6.63(t, 2.3 Hz, 1H), 3.96(t, 6.5 Hz, 4H), 3.87(s, 3H), 1.74(m, 4H), 1.45-1.30(m, 12H), 0.90(t, 7.1 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 166.91 ppm, 160.11, 131.76, 107.56, 106.51, 68.25, 52.08, 31.51, 29.11, 25.65, 22.55, 13.97. ES+ HR-MS 337.2378 (M+H). Elem. Anal.: Calc.: C 71.39, H 9.59 %. Found: C 71.73, H 9.81 %

3,5-Bis-hexyloxy-benzoic acid (19). The methyl ester (**18**, 2.499 g, 7.427 mmol) and sodium hydroxide (2.395 g, 59.86 mmol) were dissolved in a mixture of 45 mL methanol, 15 mL THF, and 15 mL deionized water with stirring. Three drops of Aliquat 336 phase-transfer catalyst were added the mixture was heated to 60°C for 18 hours. The cooled solution was concentrated under reduced pressure, neutralized with 6 M hydrochloric acid (~ 6 mL), and extracted 3 x 25 mL ethyl acetate. The combined organic extracts were dried over Na2SO4 and the solvent was removed under reduced

pressure. The resulting crude product was purified by column chromatography using 8:2 hexanes : ethyl acetate to afford 2.246 g (93.8 %) of pure product. ^{1}H NMR (Acetone-d_6): δ 7.16 ppm(d, 1.8 Hz, 2H), 6.70(s, 1H), 4.01(t, 6.4 Hz, 4H), 1.77(m, 4H), 1.55-1.25(m, 12H), 0.90(t, 6.5 Hz, 6H). ^{13}C NMR (Acetone-d_6): δ 207.21 ppm, 162.21, 134.24, 109.53, 107.66, 69.85, 33.30, 30.90, 27.41, 24.27, 15.31. ES+ HR-MS 345.2042 (M+Na). Elem. Anal.: Calc.: C 70.77, H 9.38 %. Found: C 70.74, H 9.25 N 0.10 %

3,5-Bis-(methyl succinate)-benzoic acid 2,2,2-trichloro-ethyl ester (21). An oven-dried flask was charged with dicyclohexylcarbodiimide (DCC, 8.030 g, 38.92 mmol) and mono-methyl succinate (3.962 g, 29.99 mmol), which were mechanically mixed and dried under reduced pressure. These were then dissolved in 100 mL dry dichloromethane under argon and allowed to react for 15 min. DMAP (0.552 g, 4.518 mmol) was then added and the mixture allowed to react for an additional 10 min. To this was added dropwise 10 mL of a 1 M solution of 3,5-dihydroxy-benzoic acid 2,2,2-trichloroethyl ester (**20**) in dichloromethane. The reactants were stirred at room temperature for 72 hours. The reaction mixture was filtered through a glass frit, washing with excess deionized water and dichloromethane, and then extracted 2 x 50 mL dichloromethane. The combined organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude material was purified via column chromatography in 6:4 ethyl acetate : hexanes, after loading the material in 7:3 ethyl acetate : hexanes, to afford 4.617 g (89.9%) pure product. ^{1}H NMR ($CDCl_3$): δ 7.72 ppm(d, 2.2 Hz, 2H), 7.22(t, 2.2 Hz, 1H), 4.95(2, 2H), 3.71(s, 6H), 2.89(m, 4H), 2.74(m, 4H). ^{13}C NMR ($CDCl_3$): δ 172.26 ppm, 170.22, 163.15, 150.97, 130.69, 121.05, 120.58, 94.64, 74.59, 51.97, 29.17, 28.70. ES+ HR-MS 534.9960 (M+Na). Elem. Anal.: Calc.: C 44.42, H 3.73 %. Found: C 44.56, H 3.59 %

3,5-Bis-(methyl succinate)-benzoic acid (22). The 2,2,2-trichloroethyl ester (**21**, 1.347 g, 2.622 mmol) was dissolved in a mixture of 5 mL THF and 5 mL glacial acetic acid, to which zinc dust (1.198 g, 18.32 mmol) was added with stirring. The reaction was monitored by TLC, which indicated complete reaction after 3 hours. The mixture was then filtered, washing with ethyl acetate and deionized water,

and brought to pH ~ 8 with sodium bicarbonate. This was extracted 3 x 50 mL ethyl acetate, and the water layer was then acidified to pH ~ 6 with 6 M hydrochloric acid. The acidic solution was then extracted 3 x 75 mL ethyl acetate, and these organic extracts were dried over Na_2SO_4 and the solvent removed under reduced pressure. The crude material was purified via column chromatography in 6:4 ethyl acetate : hexanes, after loading the material in pure ethyl acetate, to afford 0.789 g (79.1 %) of pure product. ^{1}H NMR (Acetone-d_6): δ 7.68 ppm(d, 2.2 Hz, 2H), 7.22(t, 2.2 Hz, 1H), 3.67(s, 6H), 2.96(m, 4H), 2.75(m, 4H). ES+ HR-MS 405.0798 (M+Na). Elem. Anal.: Calc.: C 53.41, H 4.75 %. Found: C 53.28, H 4.70 %

Synthesis of SJLD Chromophores

2-[3-Cyano-4-(2-{5-[2-(4-diethylaminophenyl)vinyl]-[bi(ProDOT(CH$_2$OH)$_2$)-yl]}-vinyl)-5,5-dimethyl-5H-furan-2-ylidene]-malononitrile (tetra-ol, 13). In an oven-dried flask, **OLD-5** (0.891 g, 0.672 mmol) was dissolved in 60 mL of dry THF and cooled in an ice-water bath. Tetrabutylammonium fluoride (TBAF, 5.375 mL, 1 M in THF) was slowly added to the solution. The ice bath was then removed and the reaction was allowed to stir for 2.5 hours while monitoring by TLC. If necessary, an additional 2.688 mL TBAF was added, and the reaction allowed to stir for an additional 1 hour to ensure complete reaction. The reaction was then quenched with 50 mL of deionized water, concentrated under reduced pressured, and the product was isolated via filtration. The crude material was purified via filtration from hot methanol to yield relatively pure product (0.501 g, 85.8%), which was used without further purification. ^{1}H NMR (acetone-d_6): δ 8.08(d, J = 15.7 Hz, 1H), 7.41(d, 8.9 Hz, 2H), 7.05(d, 16.2 Hz, 1H), 6.91(d, 16.4 Hz, 1H), 6.75(d, 15.9 Hz, 1H), 6.70(d, 8.9 Hz, 2H), 4.36-4.02(m, 8H), 3.79(m, 8H), 3.38(m, 4H), 1.82(s, 6H), 1.60(m, 4H), 1.40(m, 4H), 0.96(t, 6H).

General procedure for synthesis of the pseudo-discotic chromophores

An oven-dried flask was charged with dicyclohexylcarbodiimide (DCC, 0.185 g, 0.898 mmol) and the appropriate dendron carboxylic acid (0.690 mmol), which were mechanically mixed and dried under reduced pressure. These were then dissolved in 5 mL dry dichloromethane under argon and allowed to react for 15 min. Dimethylaminopyridine (DMAP, 0.013 g, 0.104 mmol) was then added and the

mixture allowed to react for an additional 10 min. To this was added dropwise a solution of the tetra-ol (**13**, 0.100 g, 0.115 mmol) in 2 mL dichloromethane and 0.25 mL DMF. The reactants were stirred at room temperature for 72 hours. The reaction mixture was then diluted with 50 mL dichloromethane and extracted 2 x 50 mL deionized water. The organic fraction was dried over Na_2SO_4 and the solvent was removed under reduced pressure. This crude material was initially purified by filtration from hot methanol, and then further purified via column chromatography.

SJLD-1. 50.0 mg (0.0575 mmol) **13**, 175 mg (0.345 mmol) **16**, 94.0 mg (0.456 mmol) DCC, 9.0 mg (0.074 mmol) DMAP. Column chromatography in 98:2 dichloromethane : acetone afforded 98.0 mg (60.5%) pure product. ^{1}H NMR ($CDCl_3$): δ 7.77(d, 15.6 Hz, 1H), 7.32(d, 8.8 Hz, 2H), 7.24(s, 8H), 6.96(d, 16.0 Hz, 1H), 6.86(d, 15.9 Hz, 1H), 6.58(d, 8.2 Hz, 2H), 6.46(d, 15.8 Hz, 1H), 4.72-4.41(m, 16H), 3.89(m, 24H), 3.29(m, 4H), 1.76-1.33(m, 122H), 0.92(m, 78H). MALDI MS 2823.79 (M^+). Elem. Anal.: Calc.: C 72.30, H 9.28 %, N 1.98 %. Found: C 74.14, H 9.83 % N 1.69 %.

SJLD-2. 100 mg (0.115 mmol) **13**, 224 mg (0.695 mmol) **19**, 188 mg (0.913 mmol) DCC, 20.0 mg (0.160 mmol) DMAP. Column chromatography in 99:1 dichloromethane : acetone afforded 205 mg (85.4%) pure product. ^{1}H NMR ($CDCl_3$): δ 7.75(d, 15.3 Hz, 1H), 7.35(d, 8.9 Hz, 2H), 7.12(m, 8H), 6.98(d, 16.1 Hz, 1H), 6.87(d, 16.2 Hz, 1H), 6.65(m, 4H), 6.58(d, 9.0 Hz, 2H), 6.47(d, 15.6 Hz, 1H), 4.65-4.40(m, 16H), 3.95(t, 5.9 Hz, 16H), 3.29(t, 7.1 Hz, 4H), 1.75-1.32(m, 78H), 0.98-0.90(m, 30H). MALDI MS 2085.96 (M^+). Elem. Anal.: Calc.: C 70.22, H 7.92 %, N 2.68 %. Found: C 70.22, H 7.86 % N 2.79 %.

SJLD-3. 40.0 mg (0.0460 mmol) **13**, 110 mg (0.288 mmol) **22**, 95.0 mg (0.461 mmol) DCC, 9.0 mg (0.074 mmol) DMAP. Column chromatography in 93:7 dichloromethane : acetone afforded 60.1 mg (56.1%) pure product. ^{1}H NMR ($CDCl_3$): δ 7.80-7.65(m, 9H), 7.35(d, 9.1 Hz, 2H), 7.26-7.21(m, 4H), 6.98(d, 16.2 Hz, 1H), 6.87(d, 16.3 Hz, 1H), 6.59(d, 8.4 Hz, 2H), 6.51(d, 15.7 Hz, 1H), 4.67-4.38(m, 16H), 3.71(s, 24H), 3.29(t, 7.1 Hz, 4H), 2.88(m, 16H), 2.73(m, 16H), 1.75(s, 6H), 1.56(m, 4H), 1.40-

1.25(m, 4H), 0.96(t, 7.2 Hz, 6H). MALDI MS 2325.35 (M^+). Elem. Anal.: Calc.: C 58.86, H 5.03 %, N 2.41 %. Found: C 58.72, H 4.70 % N 2.41 %.

SJLD-4. 100 mg (0.115 mmol) **13**, 238 mg (0.712 mmol) **23**, 434 mg (2.10 mmol) DCC, 35.0 mg (0.280 mmol) DMAP. Column chromatography in 98:2 dichloromethane : acetone afforded 221 mg (90.0%) pure product. ^{1}H NMR ($CDCl_3$): δ 7.71(d, 15.7 Hz, 1H), 7.43-7.28(m, 42H), 7.24(t, 2.2 Hz, 8H), 6.97(d, 16.1 Hz, 1H), 6.89-6.79(m, 5H), 6.56(d, 8.9 Hz, 2H), 6.43(d, 15.7 Hz, 1H), 5.03(s, 16H), 4.62-4.29(m, 16H), 3.28(t, 7.1 Hz, 4H), 1.67(s, 6H), 1.55(m, 4H), 1.40-1.25(m, 4H), 0.96(t, 7.2 Hz, 6H). MALDI MS 2133.70 (M^+). Elem. Anal.: Calc.: C 73.15, H 5.48 %, N 2.62 %. Found: C 72.87, H 4.94 % N 2.04 %.

SJLD-5. 100 mg (0.115 mmol) **13**, 385 mg (0.696 mmol) **24**, 188 mg (0.913 mmol) DCC, 25.0 mg (0.200 mmol) DMAP. Column chromatography in 99:1 dichloromethane : acetone afforded 280 mg (85.4%) pure product. ^{1}H NMR ($CDCl_3$): δ 7.69(d, 15.7 Hz, 1H), 7.31(t, 2.5 Hz, 8H), 7.19(d, 9.3 Hz, 2H), 6.87(d, 16.1 Hz, 1H), 6.80-6.71(m, 5H), 6.54-6.48(m, 3H), 5.13(s, 16H), 4.65-4.45(m, 16H), 3.29(t, 8.5 Hz, 4H), 1.76(s, 6H), 1.61(m, 4H), 1.38-1.31(m, 4H), 0.97(t, 7.3 Hz, 6H). MALDI MS 2853.19 (M^+). Elem. Anal.: Calc.: C 54.71, H 2.68 %, N 1.96 %. Found: C 54.52, H 2.10 % N 1.39 %.

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