Electronic Supporting Information (ESI) for

Self-Assembling Poly(Dioxaborole)s as Blue-Emissive Materials

Weijun Niu, Mark D. Smith and John J. Lavigne*

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208; E-mail: lavigne@mail.chem.sc.edu

Contents:
(1) **Synthesis and characterization of polymer 1**
(2) **Synthesis and characterization of model compound 2**
(3) **Gel Permeation Chromatography (GPC) methods**
(4) **Solid ^{11}B NMR spectra of 1 and 2**
(5) **Single crystal X-ray structure of 2**
(6) **Powder XRD analysis of 1 and 3**
(7) **Calculated polarizabilities for a series of non-conjugated and conjugated linear oligomers**
(8) **Calculated electronic spectra for oligo(borole)s of increasing length**
(9) **Absorbance spectra of the di-boronic acid starting material, non-conjugated neopentyl glycol di-ester, 2 and 3:**

Materials

Chemicals for the synthesis of the polymer **1** were purchased from Acros and Aldrich and were used without further purification. All solvents were obtained from solvent purification systems from Innovative Technologies.

Instrumentation

Solution phase ^{1}H NMR spectra were collected on a Bruker 300 MHz spectrometer. Solid-state ^{11}B NMR spectra were collected on a Varian Inova 500 MHz spectrometer with a Doty 4 mm XC-MAS probe. Absorbance studies were performed using a Beckman Coulter 640 DU

spectrophotometer and quartz cuvets from Starna. Powder X-ray diffraction data were collected on a Rigaku DMax 2200 using Cu Kα radiation.
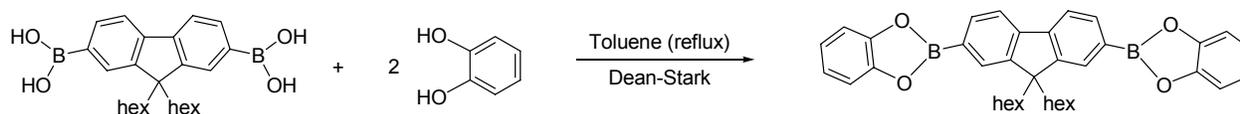
Synthesis

3   4   1
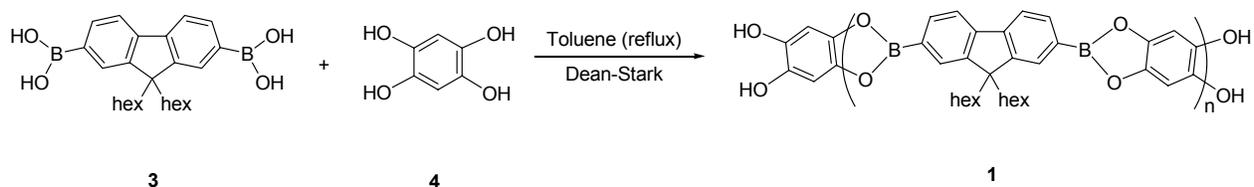
*(1) Synthesis of **1**:*   To a mixture of 0.1352 g (0.3202 mmol) of 9,9-dihexylfluorene-2,7-diboronic acid and 0.1352 g (0.3220 mmol) of freshly-prepared 1,2,4,5-tetrahydroxybenzene in a flask fitted with a Dean-Stark trap, 50 ml of distilled THF was added.   Under an argon atmosphere, this resulting solution was refluxed for 30 minutes to yield a clear light yellowish solution which was then cooled to room temperature.   Solvent THF was then removed under reduced pressure to yield a solid which is washed by distilled CH_3CN to yield a powder product (0.1437 g, 91%). ^{1}H NMR (300 MHz, DMSO-d_6, δ): 7.80-7.72 (dd, 4H, Ar H), 7.84 (s, 2H, Ar H), 6.20 (s, 2H, Ar H), 2.02-1.83 (br t, 4H, α-methylene protons from the two hexyl chains), 1.12-0.91 (m, 12H), 0.72 (t, 6H), 0.55-0.43 (m, 4H); Solid ^{11}B NMR (160.49 MHz, $BF_3 \bullet Et_2O$ at 0 ppm as the external reference and boric acid as the second reference at 19.3 ppm): 31-35 ppm.

^{1}H NMR of polymer **1**
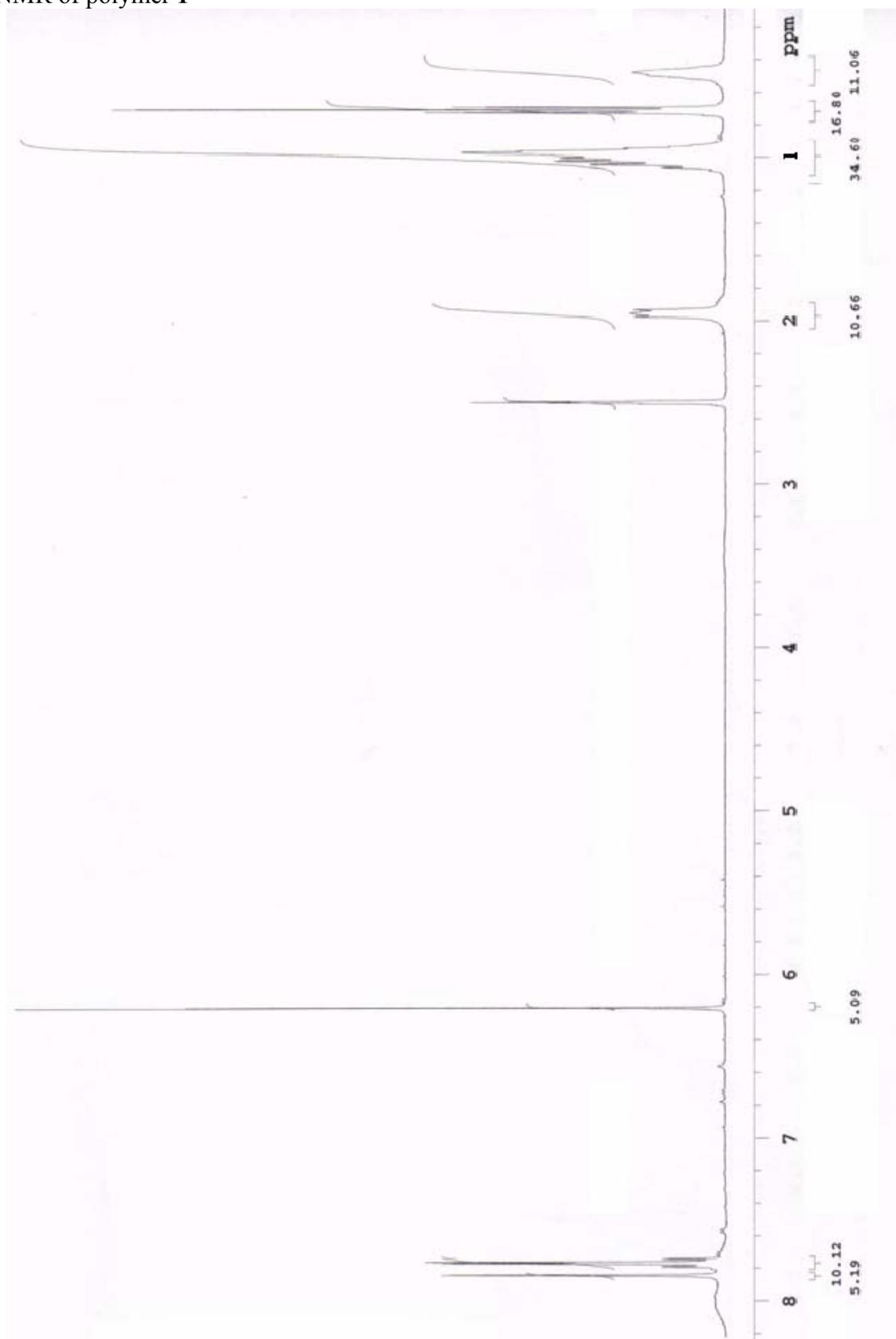
(2) Synthesis of 2: To a mixture of 0.3623 g (0.8582 mmol) of 9,9-dihexylfluorene-2,7-diboronic

acid and 0.1890 g (1.7165 mmol) of catechol in a flask fitted with a Dean-Stark trap, 55 ml of

distilled toluene was added. Under Ar protection, this resulting solution was refluxed for 18

hours to yield a clear solution which is then cooled to room temperature. Solvent toluene in this

solution was then removed under reduced pressure to form a white crystalline solid (0.4789 g).

^{1}H NMR in CDCl$_3$: 8.11 (dd, 2H, J = 9.9, 1.1 Hz), 8.09 (s, 2H), 7.90 (dd, 2H, J = 7.5, 0.6 Hz),

7.36 (4H, AA′ of AA′BB′), 7.15 (4H, BB′ of AA′BB′), 2.17-2.06 (m, 4H, α-methylene protons

from the two hexyl groups), 1.14-0.93 (m, 12H), 0.73 (t, 6H, six methyl protons from the two

hexyl groups, J = 6.9 Hz), 0.68-0.52 (m, 4H); ^{11}B NMR (160.49 MHz, CDCl$_3$, BF$_3$•Et$_2$O at 0

ppm as the external reference): 30 ppm. Solid ^{11}B NMR (160.49 MHz, BF$_3$•Et$_2$O at 0 ppm as

the external reference and boric acid as the second reference at 19.3 ppm): 28 ppm. MS calcd for

C$_{37}$H$_{40}$B$_2$O$_4$: 570.3125; found (Direct-probe): m/z 570.3141. Crystals for X-ray analysis were

obtained by the slow evaporation of a CH$_2$Cl$_2$/hexane solution of **2**.

(3) Gel Permeation Chromatography (GPC). Analyses were performed at room temperature with chloroform as the eluent, at a flow rate of 1.0 mL/min, using two Polymer Laboratories technology PLgel 5μm MIXED-D columns connected in series. The detector used is a SPD-M10 A VP Shimadzu Diode Array Detector. Calibration was performed using polystyrene standards (Polymer Laboratories for molecular weights, MW, 299 400, 143 400, 66 350, 38 100, 19 880, 9920, 4920, 2360, 1260 and 580).
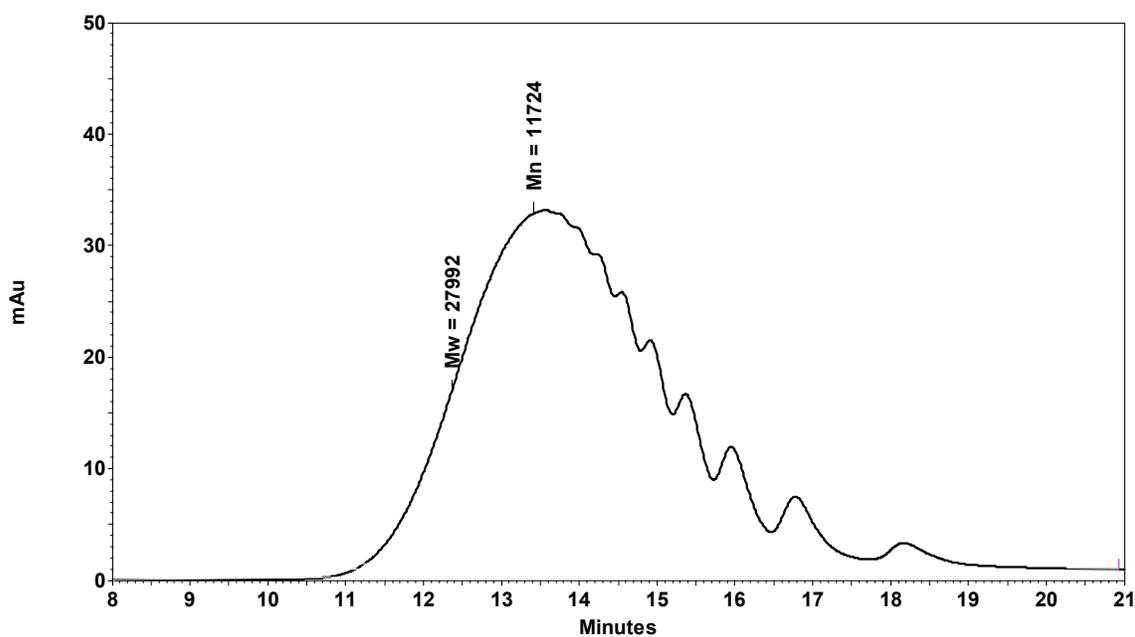

Figure S1. Typical GPC trace for a 1:10 acid:diol polymer: $M_w \approx 28,000$; $M_w/M_n = 2.4$.

(4) Solid ^{11}B NMR spectra of 1 and 2: Solid ^{11}B NMR were collected on a Varian Inova 500 MHz spectrometer with a Doty 4 mm XC-MAS probe operating at160.49 MHz, using $BF_3 \bullet Et_2O$ at 0 ppm as the external reference and boric acid as the second reference at 19.3 ppm.
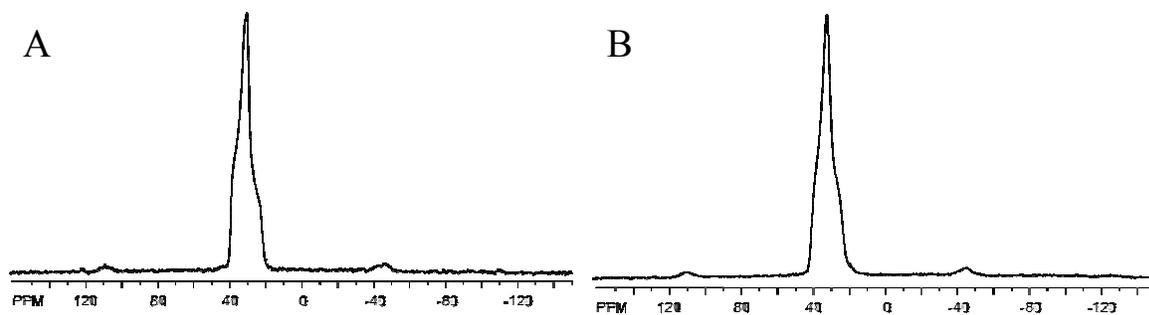

Figure S2. Solid ^{11}B NMR of model compound **2** (A) and polymer **1** (B).

(5) Single crystal X-ray structure of 2: X-ray intensity data from a colorless parallelipiped were measured at 150(2) K on a Bruker SMART APEX CCD-based diffractometer (Mo Kα radiation, λ = 0.71073 Å).[1] Raw data frame integration and Lp corrections were performed with SAINT+.[1] Final unit cell parameters were determined by least-squares refinement of 6682 reflections with I > 5(σ)I from the data set. Analysis of the data showed negligible crystal decay during collection. The data were not corrected for absorption. Direct methods structure solution, difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXTL.[2]

Systematic absences in the reflection data along with intensity statistics indicated the space group P2/n, which was eventually confirmed. The asymmetric unit consists of half of the molecule located on a two-fold rotational axis. Non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were placed in geometrically idealized positions and included as riding atoms.
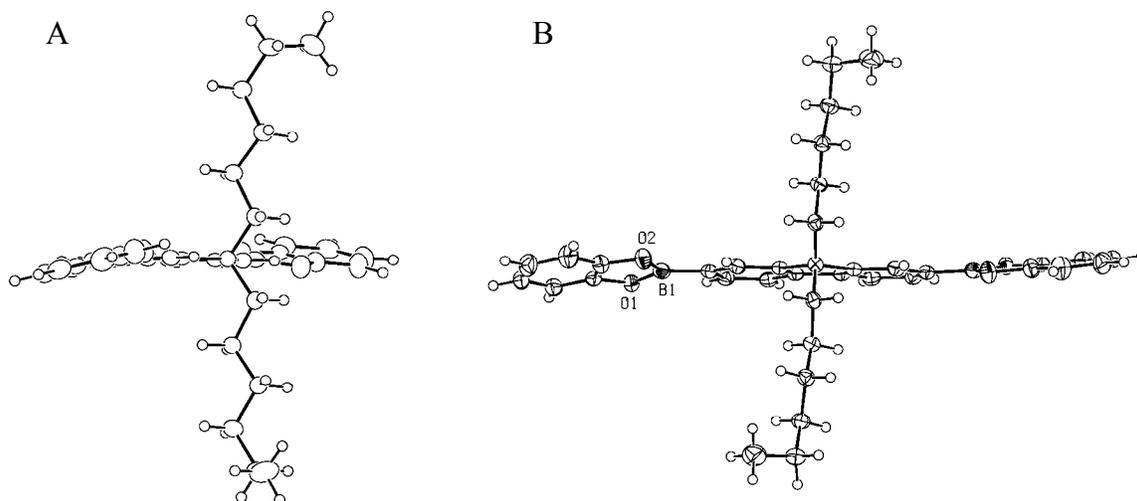

Figure S3. Edge-on views of the structure of **2** along the C2 axis, showing planarity of the fluorine-borole-phenyl system. Displacement ellipsoids drawn at the 50% probability level.

Table S1. Crystal data and structure refinement for **2**.

Empirical formula	C37 H40 B2 O4
Formula weight	570.31
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2/n
Unit cell dimensions	a = 10.2014(6) Å $\quad$ α= 90°.
	b = 10.9644(6) Å $\quad$ β= 92.5600(10)°.
	c = 13.9002(8) Å $\quad$ γ = 90°.
Volume	1553.22(15) Å^3
Z	2
Density (calculated)	1.219 Mg/m^3
Absorption coefficient	0.076 mm^{-1}
F(000)	608
Crystal size	0.52 x 0.26 x 0.08 mm^3
Theta range for data collection	1.86 to 25.12°.
Index ranges	-12<=h<=12, -13<=k<=12, -16<=l<=16
Reflections collected	12221
Independent reflections	2754 [R(int) = 0.0459]
Completeness to theta = 25.12°	99.4 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2754 / 0 / 197
Goodness-of-fit on F^2	1.079
Final R indices [I>2sigma(I)]	R1 = 0.0453, wR2 = 0.1008
R indices (all data)	R1 = 0.0533, wR2 = 0.1050
Extinction coefficient	0.0037(10)
Largest diff. peak and hole	0.235 and -0.167 e.Å^{-3}

*(6) Powder XRD analysis of **1** and **3**:* Powder X-ray diffraction data were collected on a Rigaku DMax 2200 using Cu Kα radiation. The sample was mounted in a deep well glass slide. Data were collected from 2 - 70° 2θ with steps of 0.02° with a count time of 12 s per step. There were no observable diffraction lines beyond 50° 2θ so this data was not shown.
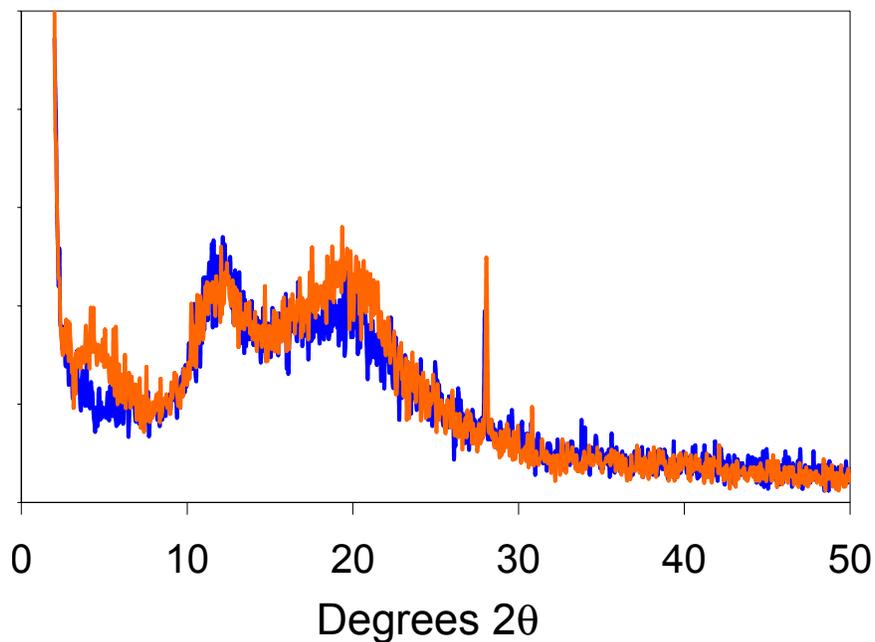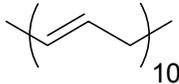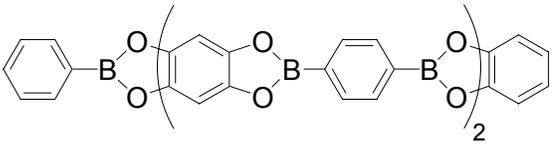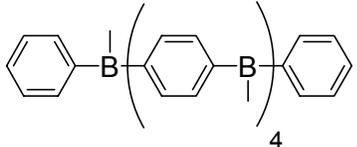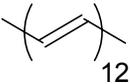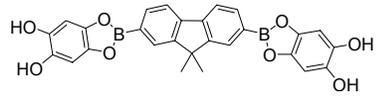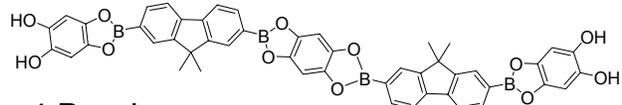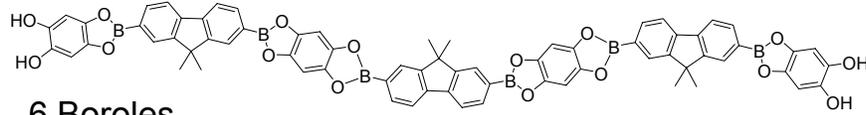

Figure S4. Powder XRD patterns for polymers **1** (orange) and **3** (blue), lacking any solid state ordering, indicative of amorphous materials.

(7) **Table S2.** *Calculated polarizabilities for a series of non-conjugated and conjugated linear polymers.*

	molecule polarizability (angstrom^3)	molecule length (angstrom)	polarizability per distance (angstrom^2)
$C_{25}H_{52}$	1651	30.5	**54.1**
	3081	33.8	**91.2**
	6209	34.2	**182**
	5493	30.5	**180**
	6944	29.2	**238**
	7545	30.4	**248**
	7295	29.9	**244**
	8523	30.9	**276**
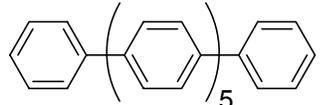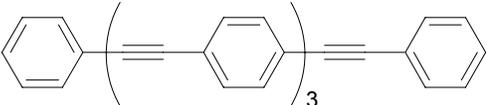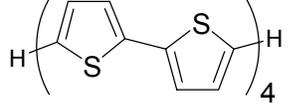
Geometry optimization based on molecular mechanics was carried out using the AMBER force field[3] in Chem3D.[4] Oligomers were forced to be planar prior to optimization and the routine biased to maintain planarity. For the optimized structures, polarizabilities were calculated using the AM1 routine[5] in *CS MOPAC PRO*.[6] Polarizability comparisons were along the long axis of each oligomer. Lengths were determined by the distance measured in *Chem3D* from the terminal heavy atoms of each chain.

(8) **Table S3.** *Calculated electronic spectra for oligo(borole)s of increasing length*

	Calculated Abs$_{max}$	Mol wt
 2 Boroles	407	635
 4 Boroles	414	1125
 6 Boroles	421	1619

Geometry optimization based on molecular mechanics was carried out at 10K using the AMBER force field[3] in *HyperChem*.[7] Oligomers were forced to be planar prior to optimization and the routine biased to maintain planarity. For the optimized structures, electronic spectra were generated using the routine ZINDO/1 following a singly excited configuration interaction (CI) calculation with the semi-empirical method (energy criterion = 10 eV). The numbers of occupied and unoccupied orbitals set in the single point CI calculations were both set equal to ten. The hexyl substituents on the fluorene unit were truncated to methyl groups to reduce the cost of the calculation.

(9) Absorbance spectra of the di-boronic acid starting material, non-conjugated neopentyl glycol di-ester, 2 and 3:
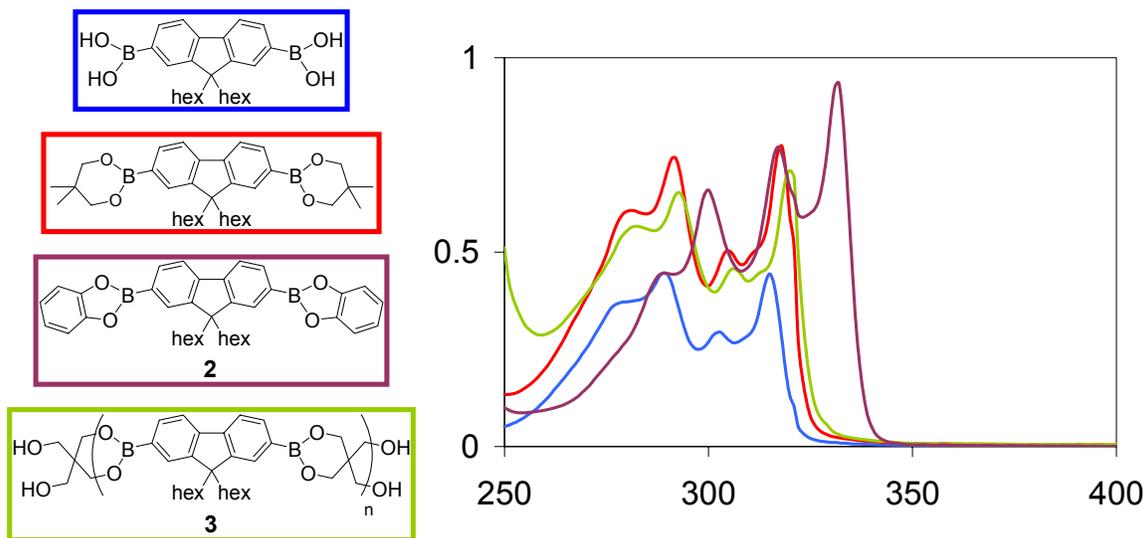

Figure S5. Absorption spectra for the di-boronic acid starting material (blue), non-conjugated neopentyl glycol di-ester (red), conjugated model compound **2** (purple), and non-conjugated polymer **3** all at 1 x 10^{-5} M (polymers based on repeat concentration).

1   *SMART* Version 5.625 and *SAINT+* Version 6.22. Bruker Analytical X-ray Systems, Inc.: Madison, Wisconsin, 2001.

2   Sheldrick, G. M. *SHELXTL* Version 6.1; Bruker Analytical X-ray Systems, Inc.: Madison, Wisconsin, 2000.

3   Cornell, W. D.; Cieplak, P.; Bayly, C. I.; Gould, I. R.; Merz, K. M.; Ferguson, D. M.; Spellmeyer, D. C.; Fox, T.; Caldwell, J. W.; Kollman, P. A. *J. Am. Chem. Soc.* **1995**, *117*, 5179-5197.

4   *Chem3D*, CambridgeSoft Corp.: Cambridge, MA., 2000.

5   Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart J. J. P., *J. Am. Chem. Soc.* **1985**, *107*, 3902-3909

6   *CS MOPAC Pro – MOPAC 2000*, Version 6.0; CambridgeSoft Corp.: Cambridge, MA., 2000

7   *HyperChem*, version 7.0; HyperCube Inc.: Gainesville, FL., 2002.