

Electronic Supplementary Information for

Liquid Crystalline behavior of tetraaryl derivatives of benzo[*c*]cinnoline, tetraazapyrene, phenanthrene, and pyrene: The effect of heteroatom and substitution pattern on phase stability¹

Monika J. Sienkowska,^a John M. Farrar,^a Fan Zhang,^b Sharat Kusuma,^a Paul A. Heiney,^b
and Piotr Kaszynski^{*a}

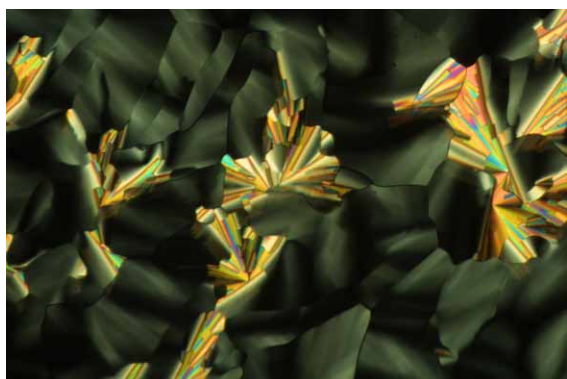
^a *Organic Materials Research Group Department of Chemistry, Vanderbilt University, Nashville, TN 37235, USA.*

^b *Department of Physics and Astronomy, University of Pennsylvania, Philadelphia, PA 19104.*

Table of Content:

1. Optical textures for columnar phasesS2
2. XRD data for 1–3S3
3. DSC Data for 2cS6
4. Binary MixturesS8
5. Computed FMO energiesS8
6. Experimental red-ox data for selected compoundsS9
7. Synthetic DetailsS10
8. Archive data for MP2/6-31G(d) optimizations of 21a–21cS19
9. ReferencesS22

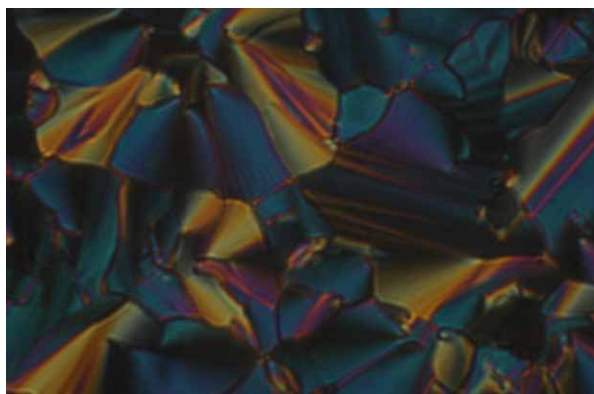
1. Optical textures for columnar phases



a



b)



c)

Figure 1. Optical textures of **1a** (a) at 155 °C; (b) **2c** at 170 °C (no shutter used); (c) **4c** at 75 °C. All textures were obtained upon cooling. Magnification $\times 300$.

2. XRD data for 1-3

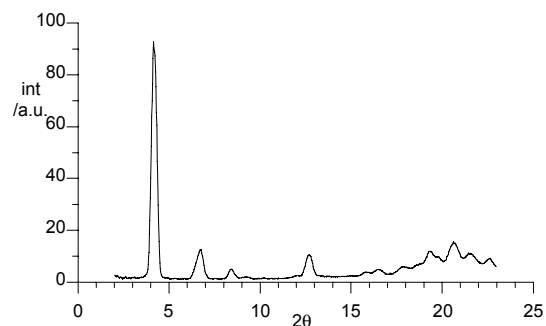


Figure 2. X-ray diffraction pattern for **1b** at 38 °C

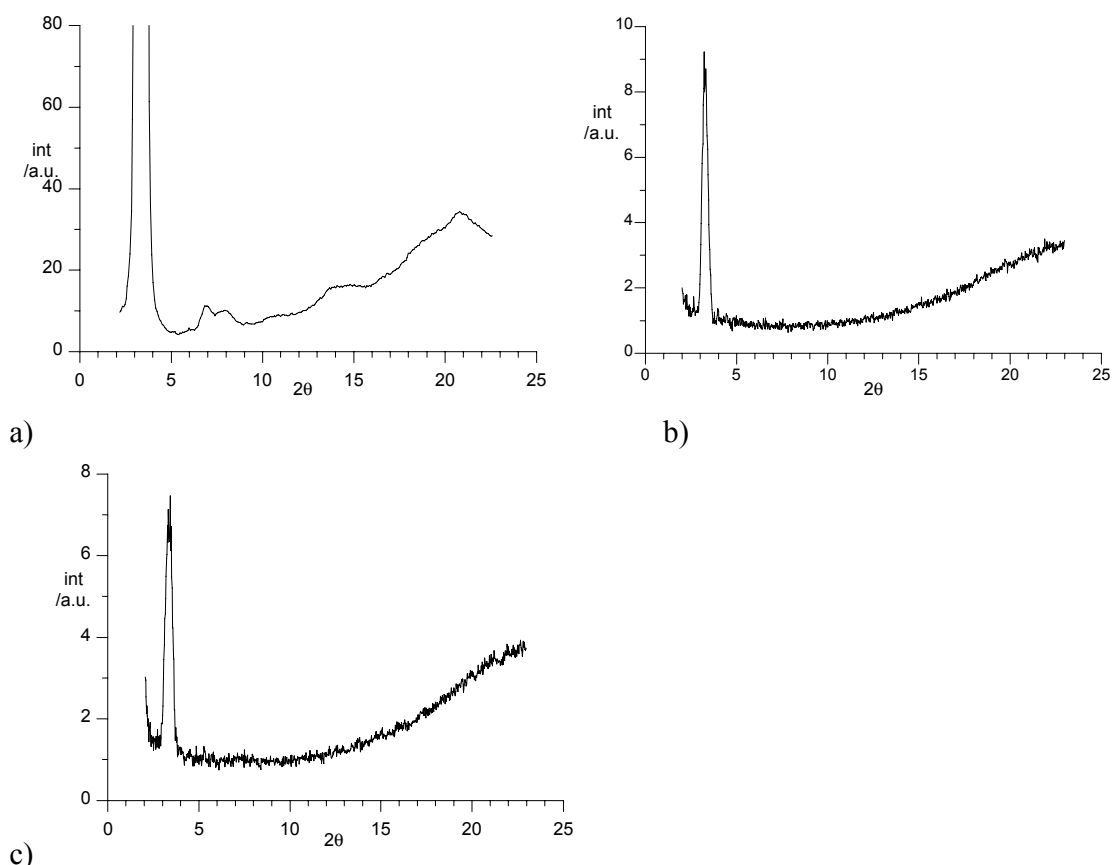


Figure 3. X-ray diffraction patterns for **1c**: a) RT before heating, b) at 117 °C, c) RT after cooling.

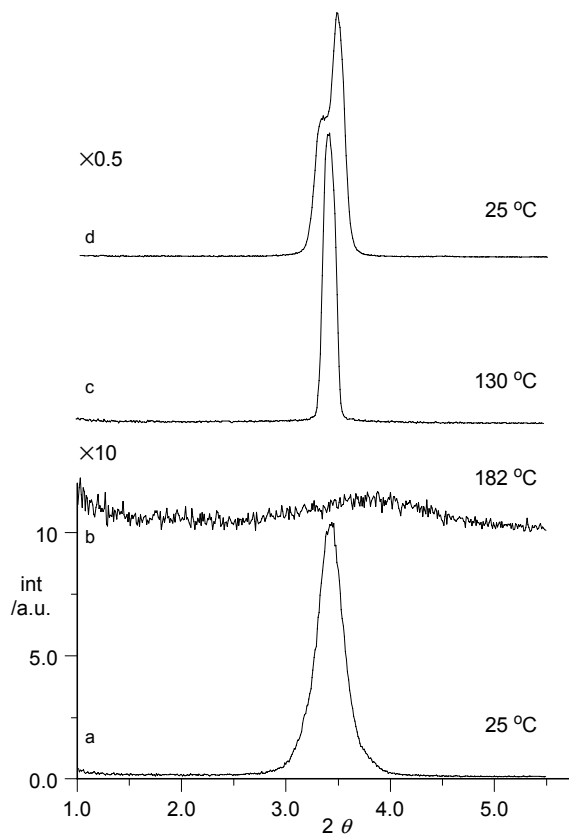


Figure 4. Small-Angle X-ray diffraction patterns for **1c** a) 25 °C before heating (crystalline), b) 182 °C (isotropic), c) 130 °C (Col_h), d) 25 °C after cooling.

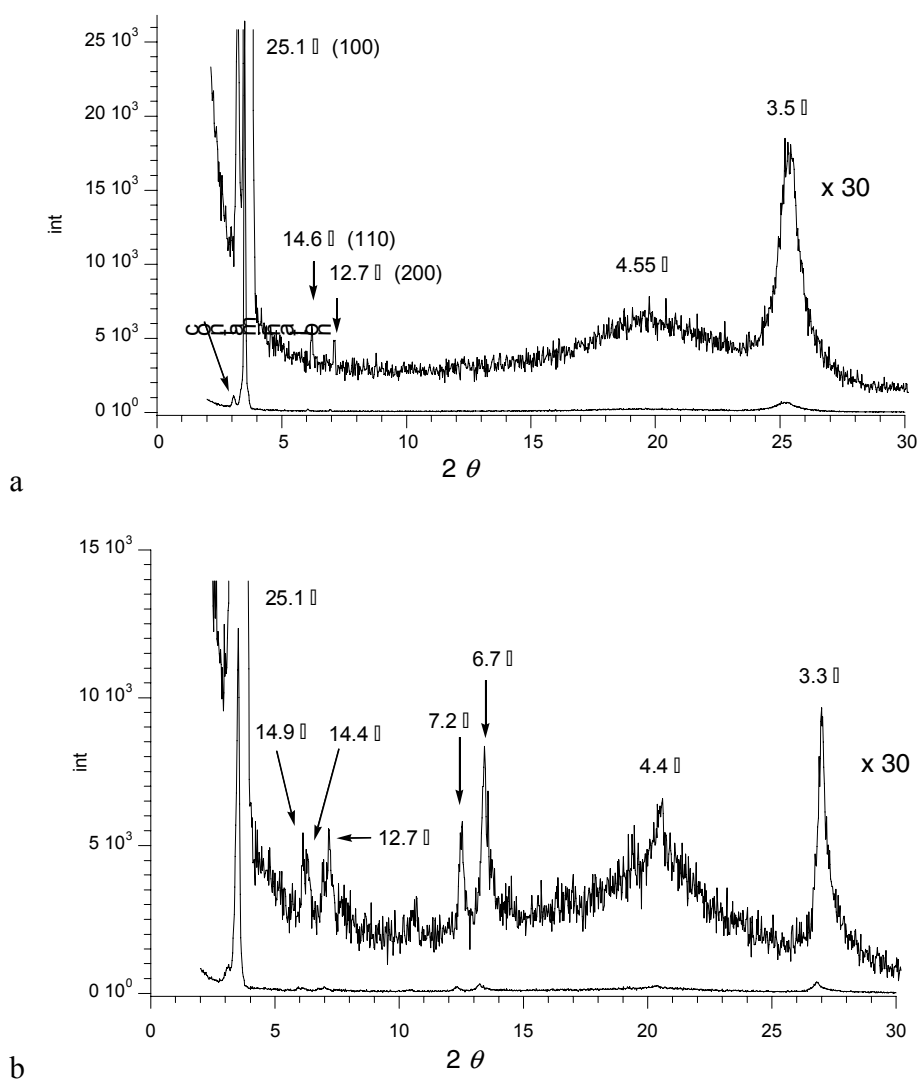


Figure 5. X-ray diffraction data for **1c** at: a) 130 °C, b) 50 °C. Data were collected with Scitag diffractometer. The small peak at the left side of the 100 peak results from spectral contamination (K_β line) of the incident beam.

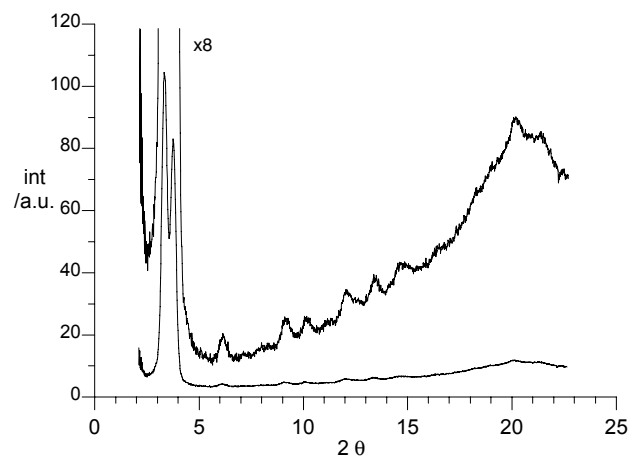


Figure 6. X-ray diffraction pattern for tetraazapyrene **2c** at 29 °C.

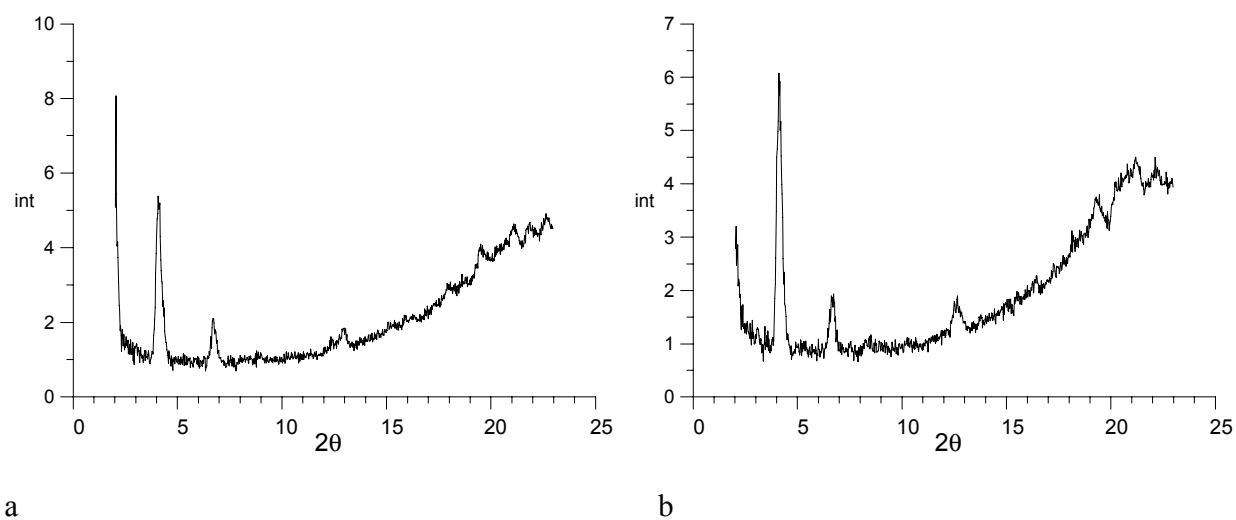


Figure 7. X-ray diffraction patterns for phenanthrene **3b**: a) RT before heating, b) at 80 °C.

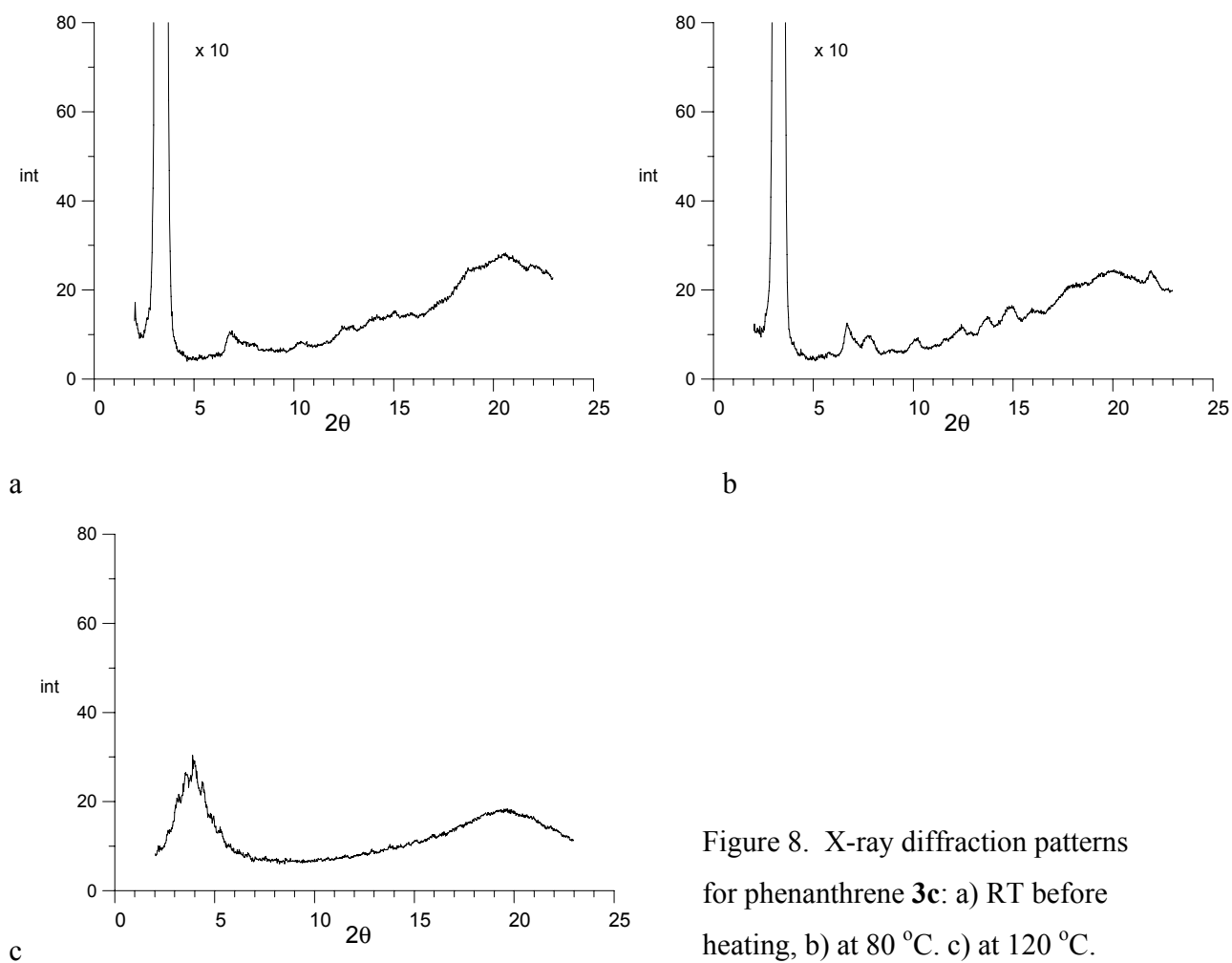


Figure 8. X-ray diffraction patterns for phenanthrene **3c**: a) RT before heating, b) at 80 °C. c) at 120 °C.

3. DSC Data for **2c**

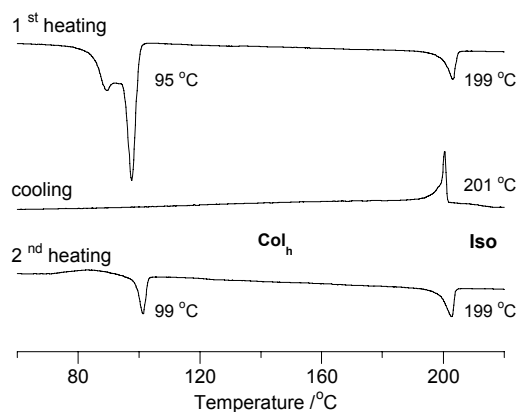


Figure 9. DSC traces of tetraazapyrene **2c**. The heating rate was 5 °C min⁻¹.

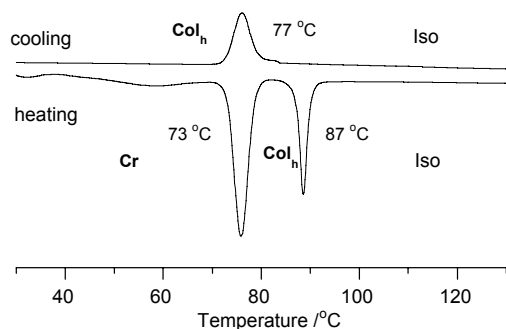


Figure 10. DSC traces of pyrene **4c**. The heating rate was 10 °C min⁻¹.

4. Binary mixtures

Binary mixtures were prepared in the following way: appropriate amounts of compounds were dissolved in a small amount of CH₂Cl₂. Solvent was evaporated at ~ 50 °C and the resulting mixture was vacuum dried at 80 °C under reduced pressure. The compounds were analyzed by DSC and the peak of the transition was taken as the clearing temperature.

Table 1. Mole fractions and clearing temperatures for binary mixtures.

1d in 1c		2d in 2c		4d in 4c	
Mol fraction	Clearing Temp Peak / °C	Mol fraction	Clearing Temp Peak / °C	Mol fraction	Clearing Temp Peak / °C
0.00	168	0.00	201	0.000	90
0.103	157	0.109	121	0.091	82
0.194	140	0.205	144	0.167	79

5. Computed FMO energies

Table 2. MP2/6-31G* FMO energy for parent compounds at fully optimized geometry.

Compound	Symmetry	HOMO eV	LUMO eV	ΔE eV
Phenanthrene 3a	C _{2v}	-7.52 B ₁	2.54 A ₂	10.06
Benzo[<i>c</i>]cinnoline 1a	C _{2v}	-8.39 A ₂	1.54 A ₂	9.94
Pyrene 4a	D _{2h}	-6.87 B _{1G}	1.80 A _u	8.66
Tetraazapyrene 2a	D _{2h}	-8.26 B _{1G}	0.30 A _u	8.56
tiphenylene	D _{3h}	-7.61 E''	2.54 E''	10.15
hexaazatriphenylene	D _{3h}	-8.89 E''	1.46 E''	10.35

6. Experimental red-ox data for selected compounds

The computed orbital energies collected in Table 2 provide indicate a trend in the expected electrochemical properties of the compound. The validity of this trend is supported by the experimental values that characterize the gain or loss of an electron. Thus, ionization potentials, electron affinity, and redox potentials available for compounds listed in Table 2 (and shown in Figure 10) are collected in Table 3.

A comparison of the data in Tables 2 and 3 shows a nearly linear relationship between the theoretical and (available) experimental values. This is consistent with many other similar analyses found in the literature including recent studies of discotic liquid crystals.²

Table 3. Experimental ionization potential (I_p), electron affinity (EA), and redox potentials for selected compounds.

Compound	I_p /eV	$E_{1/2}$ (ox) /V	EA /eV	$E_{1/2}$ (red) /V
Phenanthrene, 3a	7.86 ^a	+1.50 ^b +1.45 ^c	na	-2.48 ^d -2.88 ^c
Benzo[c]cinnoline, 1a	8.3 ^e		0.89 ^f	-1.554 ^g
Pyrene, 4a	7.41 ^h	+1.16 ^b +1.12 ^c +1.28 ^d	0.45 ⁱ 0.59 ^j	-2.09 ^d -2.49 ^c
Tetraazapyrene, 2a	na	na	na	na
Triphenylene	7.87 ^a	+1.55 ^b +1.50 ^c	0.285 ^j	-2.87 ^c
Hexaazatriphenylene	na	na	na	-1.42 ^k

^a PES; D. Biermann, W. Schmidt, *J. Am. Chem. Soc.* 1980, **102**, 3163. ^b 2.0 M NaClO₄ in MeCN vrs SCE; E. S. Pysh, N. C. Yang, *J. Am. Chem. Soc.* 1963, **85**, 2124. ^c MeCN, 0.1 M TEAP, vrs Ag/AgClO₄ 0.1; M, B. Case, N. S. Hush, R. Parsons, M. E. Peover, *J. Electroanal. Chem.* 1965, **10**, 360. ^d T. Kubota, K. Kano, B. Uno, T. Konse, *Bull. Chem. Soc. Jpn* 1987, **60**, 3865. ^e O. Dolgounitcheva, V. G. Zakrzewski, J. V. Ortiz, *J. Phys. Chem.* 1997, **101**, 8554. ^f G. W Dillow, P. Kebarle, *Can J. Chem.* 1989, **67**, 1628. ^g 0.1 M TEAP in MeCN vrs SCE; S. Millefiori, *J. Heterocycl. Chem.* 1970, **7**, 145. ^h PES, E. Clar, J. M. Robertson, R. Schlogl, W. Schmidt, *J. Am. Chem. Soc.* 1981, **103**, 1320. ⁱ G.-Z Li, H. S. Kim, S. Guan, A. G. Marshall *J. Am. Chem. Soc.* 1997, **119**, 2267. ^j D. D. Tanner, N. Deonarian, A. Kharrat. *Can. J. Chem.* 1989, **67**, 171, and references therein. ^k 0.1 M TBAP in MeCN vrs SCE; L. Tan-Sien-Hee, A. Kirsch-De Mesmaeker, *J. Chem. Soc. Dalton Trans.* 1994, 3651.

7. Synthetic Details

All NMR spectra were obtained on Bruker at 300 MHz (^1H) and 75 MHz (^{13}C) instrument in CDCl_3 . Chemical shifts were referenced to TMS (^1H) or solvent (^{13}C). IR spectra were recorded for neat samples (liquid or microcrystalline) on NaCl plates by using an ATI Mattson Genesis Series FTIR. Mass spectrometry was acquired using a HP 5890 Series II GC with attached 5971 Series MS in EI mode with the maximum m/z range of 600. Elemental Analysis was provided by Atlantic Microlabs. FAB/MS spectrometry was performed at University of Notre Dame, IN. UV spectra were recorded in cyclohexane on a Hitachi, U-3000 spectrophotometer. Molar extinction coefficients were established by plotting absorbance vrs concentration for each compound for selected wavelength: 246 nm for **1b**, 356 nm for **2b**, 279 nm for **3b**, and 304 nm for **4b**.

Preparation of 1-3 by Suzuki coupling. General procedure.³ A mixture of **1e**,⁴ **2e**, **3e**,⁵ or **4e**⁶ (1 mmol), boronic ester **5** (4.4 mmol), $\text{Pd}(\text{Ph}_3\text{P})_4$ (0.2 mmol), 2M aqueous solution of Na_2CO_3 (4 mL), EtOH (4 mL), and toluene (40 mL) was refluxed for 24-72 hrs in inert atmosphere until a single major product was observed by TLC. The reaction mixture was cooled, Et_2O was added, and the organic layer was separated and dried (Na_2SO_4). The solvent was evaporated and the crude product was passed through a silica gel plug with hexanes/ CH_2Cl_2 mixture in 2:1 ratio. The product was isolated in 20%-70% yield by liquid chromatography (hexanes followed by hexanes/ CH_2Cl_2) with increasing polarity of the eluent. The product was additionally purified by recrystallization, and its purity was confirmed by analytical HPLC.

Alternatively DME (40 mL) was used as a solvent instead of toluene. The yields of products were increased to 65%-80%.

1,3,6,8-Tetraaryl-4,5,9,10-tetraazapyrene (2b–2d). General procedure. Compounds **2b–2d** were prepared according to the modified literature procedure for the preparation of **2a**.⁷ Tetraarylated tetranitrobiphenyl **8** (1 mmol) was suspended in *n*-propanol (10 mL). 1M NaOH (1 mL) was added followed by freshly activated Raney Ni in absolute EtOH. The reaction mixture was hydrogenated under normal atmosphere until the starting material was not observed on TLC. Raney Ni was carefully filtered off, the solvent was evaporated, and the crude product was purified on a silica gel column

(eluent: hexanes/CH₂Cl₂ mixture). The chromatographic purification was followed by recrystallization from an EtOH/toluene mixture to give the product in yields in the range 20% to 29%.

2,4,7,9-Tetrakis(4-octyloxyphenyl)benzo[c]cinnoline (1b). The product was obtained in 80% yield as bright yellow crystals: mp (DSC) 133 °C; ¹H NMR δ 0.91 (t, *J* = 6.7 Hz, 12H), 1.31-1.51 (m, 40H), 1.79-1.90 (m, 8H), 4.05 (t, *J* = 6.0 Hz, 4H), 4.07 (t, *J* = 6.0 Hz, 4H), 7.05 (d, *J* = 8.8 Hz, 4H), 7.09 (d, *J* = 8.8 Hz, 4H), 7.80 (d, *J* = 8.8 Hz, 4H), 7.81 (d, *J* = 8.7 Hz, 4H), 8.09 (d, *J* = 1.8 Hz, 2H), 8.76 (d, *J* = 1.9 Hz, 2H); IR 1177 and 1245 (C-O-C), 1510, 1577, 1605 cm⁻¹; UV-vis (cyclohexane) λ_{max} (log ε): 246 (4.86), 279 sh (4.58), 310 (4.54), 373 (4.46). Anal Calcd. for C₆₈H₈₈N₂O₄: C, 81.88; H, 8.89; N, 2.81. Found: C, 82.01; H, 9.11; N, 2.80.

2,4,7,9-Tetrakis(3,4-dioctyloxyphenyl)benzo[c]cinnoline (1c). The product was isolated as a yellow solid: mp (DSC) 92 °C; ¹H NMR δ 0.84-0.92 (m, 24H), 1.26-1.55 (m, 80H), 1.78-1.93 (m, 16H), 4.04-4.15 (m, 16H), 7.03 (d, *J* = 8.3 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 7.34-7.45 (m, 8H), 8.06 (d, *J* = 1.3 Hz, 2H), 8.74 (d, *J* = 1.4 Hz, 2H); IR 1250 (C-O-C), 1512 cm⁻¹. Anal Calcd. for C₁₀₀H₁₅₂N₂O₈: C, 79.53; H, 10.14; N, 1.85. Found: C, 79.23; H, 10.22; N, 1.86.

2,4,7,9-Tetrakis(3,5-dioctyloxyphenyl)benzo[c]cinnoline (1d). The product was obtained in 76% yield as a yellow oil: ¹H NMR δ 0.85-0.88 (m, 24H), 1.27-1.50 (m, 80H), 1.78 (quintet, *J* = 7.8 Hz, 8H), 1.84 (quintet, *J* = 7.6 Hz, 8H), 3.99 (t, *J* = 6.5 Hz, 8H), 4.05 (t, *J* = 6.5 Hz, 8H), 6.56 (t, *J* = 2.2 Hz, 2H), 6.57 (t, *J* = 1.8 Hz, 2H), 6.91 (d, *J* = 2.2 Hz, 4H), 6.92 (d, *J* = 2.1 Hz, 4H), 8.09 (d, *J* = 1.6 Hz, 2H), 8.80 (d, *J* = 1.6 Hz, 2H); IR 1167 (C-O-C), 1592 cm⁻¹. Anal Calcd. for C₁₀₀H₁₅₂N₂O₈: C, 79.53; H, 10.14; N, 1.85. Found: C, 79.28; H 10.28; N, 1.88.

2,4,7,9-Tetrabromobenzo[c]cinnoline (1e).^{4,8} Compound **1e** was prepared by a modified literature procedure.⁴ Commercially available 2,2'-dinitrobiphenyl (**9**, 20.16 g, 0.083 mol) was dissolved in a mixture of EtOAc (225 mL), EtOH (75 mL), and PtO₂ (0.16 g) in a hydrogenation bottle. The reactor was charged with H₂ at 40-45 psi. After 6 hrs, the pressure stabilized and the catalyst was filtered under N₂, and the solution was concentrated to yield 15.31 g of yellow-brown crystals of diamine **10**.

The crude diamine was dissolved in AcOH (150 mL). Concentrated HCl (7 mL) was added followed by dropwise addition of Br₂ (18 mL, 0.341 mol) in AcOH (50 mL) with cooling over 30 min, and the mixture was stirred overnight. The solution was filtered to yield a yellow solid, which was neutralized with aq. NaHCO₃. The solid turned a lavender color upon neutralization and was filtered to give 26.70 g (64% yield based on **9**) of 2,2'-diamino-3,3',5,5'-tetrabromobiphenyl (**11**). A sample of the product (5.02 g, 0.01 mol) and peracetic acid (32%, 7 mL, 0.03 mol) was made into slurry in AcOH (50 mL). This mixture was warmed to 50 °C and left to stir. The solution turned green. The reaction was cooled, and a green-yellow solid was filtered off, washed with water, dried, and recrystallized from AcOH to give 4.40 g (88% yield) of **1e** as a yellow solid: mp 299 °C (lit.⁴ mp 300 °C); ¹H NMR (C₆D₆) δ 7.53 (d, *J* = 1.7 Hz, 2H), 7.79 (d, *J* = 1.8 Hz, 2H); EI MS *m/z* 500, 498, 496, 494, 492 (M, 100, 1:4:6:4:1), 310, 308, 306 (50, 1:2:1).

1,3,6,8-Tetrakis(4-octyloxyphenyl)-4,5,9,10-tetraazapyrene (2b). Mp (DSC) 161 °C; ¹H NMR δ 0.91 (t, *J* = 6.8 Hz, 12H), 1.20-1.54 (m, 40H), 1.86 (quintet, *J* = 7.0 Hz, 8H), 4.09 (t, *J* = 6.5 Hz, 8H), 7.14 (d, *J* = 8.8 Hz, 8H), 8.11 (d, *J* = 8.7 Hz, 8H), 8.62 (s, 2H); IR 1177 and 1248 (C-O-C), 1510, 1604 cm⁻¹; UV-vis (cyclohexane) λ_{max} (log ε): 233 (4.77), 242 (4.76), 268 (4.57), 273 (4.58), 305 sh (4.23), 356 (4.42), 414 sh (4.40), 439 (4.58), 462 (4.64). Anal Calcd. for C₆₈H₈₆O₄N₄: C, 79.80; H, 8.47; N, 5.47. Found: C, 80.00; H, 8.64; N, 5.47.

1,3,6,8-Tetrakis(3,4-dioctyloxyphenyl)-4,5,9,10-tetraazapyrene (2c). Mp (DSC) 95 °C; ¹H NMR δ 0.86 (t, *J* = 6.1 Hz, 12H), 0.90 (t, *J* = 6.6 Hz, 12H), 1.25-1.50 (m, 80H), 1.82-1.95 (m, 16H), 4.13 (t, *J* = 6.5 Hz, 8H), 4.14 (t, *J* = 6.5 Hz, 8H), 7.12 (d, *J* = 8.4 Hz, 4H), 7.68 (d, *J* = 2.0 Hz, 4H), 7.74 (dd, *J*₁ = 8.3 Hz, *J*₂ = 2.0 Hz, 4H), 8.62 (s, 2H); IR 1139 and 1270 (C-O-C), 1516 cm⁻¹. Anal Calcd. for C₁₀₀H₁₅₀N₄O₈: C, 78.18; H, 9.84; N, 3.65. Found: C, 78.26; H, 10.06; N, 3.47.

1,3,6,8-Tetrakis(3,5-dioctyloxyphenyl)-4,5,9,10-tetraazapyrene (2d). Mp (DSC) 45 °C; ¹H NMR δ 0.87 (t, *J* = 6.7 Hz, 24H), 1.20-1.52 (m, 80H), 1.81 (quintet, *J* = 7.0 Hz, 16H), 4.04 (t, *J* = 6.5 Hz, 16H), 6.66 (t, *J* = 2.1 Hz, 4H), 7.19 (d, *J* = 2.2 Hz, 8H), 8.67 (s, 2H); IR 1168 (C-O-C), 1539 cm⁻¹. Anal Calcd. for C₁₀₀H₁₅₀N₄O₈: C, 78.18; H, 9.84; N, 3.65. Found: C, 77.54; H, 9.92; N, 3.46.

1,3,6,8-Tetrabromo-4,5,9,10-tetraazapyrene (2e). A 30% solution of peracetic acid in AcOH (0.8 mL, 3.8 mmol) was added to a suspension of tetraamine **14** (0.80 g, 1.5 mmol) in AcOH (25 mL), and the reaction mixture was stirred at 60 °C for 48 hrs. The resulting precipitate was filtered off, washed with AcOH and dried to give microcrystalline black solid. Anal Calcd. for C₁₂H₂Br₄N₄: C, 27.62; H, 0.39; N, 10.74. Found: C, 29.48; H, 1.44; N, 9.03.

The solid was washed three times with hot CHCl₃ to yield 340 mg of a black sparingly soluble solid: ¹H NMR δ 8.25 (s). Anal Calcd. for C₁₂H₂Br₄N₄: C, 27.62; H, 0.39; N, 10.74. Found: C, 28.95; H, 1.59; N, 9.12.

1,3,6,8-Tetrakis(4-octyloxyphenyl)phenanthrene (3b). Mp (DSC) 152 °C; ¹H NMR δ 0.90 (t, *J* = 6.6 Hz, 12H), 1.31-1.51 (m, 40H), 1.84 (quintet, *J* = 6.9 Hz, 8H), 4.05 (t, *J* = 6.6 Hz, 8H), 7.03 (d, *J* = 8.8 Hz, 4H), 7.06 (d, *J* = 8.9 Hz, 4H), 7.46 (d, *J* = 8.5 Hz, 4H) 7.75-7.80 (m, 8H), 8.96 (s, 2H); IR 1246 (C-O-C), 1511 cm⁻¹; UV-vis (cyclohexane) λ_{max} (log ε): 279 (4.89), 335 (4.53). Anal. Calcd for C₇₀H₉₀O₄: C, 84.46; H, 9.11. Found: C, 84.53; H, 9.20.

1,3,6,8-Tetrakis(3,4-dioctyloxyphenyl)phenanthrene (3c). Mp (DSC) 101 °C; ¹H NMR δ 0.87 (t, *J* = 6.7 Hz, 12H), 0.90 (t, *J* = 6.7 Hz, 12H), 1.26-1.51 (m, 80H), 1.78-1.89 (m, 16H), 4.01 (t, *J* = 6.6 Hz, 4H), 4.06-4.13 (m, 12H), 6.99-7.08 (m, 8H), 7.32-7.38 (m, 4H), 7.73-7.78 (m, 4H), 8.93 (s, 2H). Anal. Calcd for C₁₀₂H₁₅₄O₈: C, 81.22; H, 10.29. Found: C, 81.45; H, 10.35.

1,3,6,8-Tetrakis(4-octyloxyphenyl)pyrene (4b). Mp (DSC) 116 °C; ¹H NMR δ 0.90 (t, *J* = 6.8 Hz, 12H), 1.26-1.49 (m, 40H), 1.85 (quintet, *J* = 7.0 Hz, 8H), 4.06 (t, *J* = 6.6 Hz, 8H), 7.06 (d, *J* = 8.7 Hz, 8H), 7.57 (d, *J* = 8.7 Hz, 8H), 7.95 (s, 2H), 8.15 (s, 4H); IR 1245 (C-O-C) cm⁻¹; UV-vis (cyclohexane) λ_{max} (log ε): 204 (5.01), 229 (4.78), 256 (4.62), 304 (4.71), 390 (4.64). Anal. Calcd for C₇₂H₉₀O₄: C, 84.82; H, 8.90. Found: C, 84.73; H, 9.04.

1,3,6,8-Tetrakis(3,4-dioctyloxyphenyl)pyrene (4c). Mp (DSC) 73 °C; ¹H NMR δ 0.86 (t, *J* = 6.8 Hz, 12H), 0.90 (t, *J* = 6.6 Hz, 12H), 1.26-1.50 (m, 80H), 1.84 (quintet, *J* = 6.9 Hz, 8H), 1.88 (quintet, *J* = 6.8 Hz, 8H), 4.04 (t, *J* = 6.6 Hz, 8H), 4.10 (t, *J* = 6.7 Hz, 8H), 7.04 (d, *J* = 8.0 Hz, 4H), 7.15-7.19 (m, 8H), 7.98 (s, 2H), 8.19 (s, 4H); IR 1249 (C-O-C) cm⁻¹; UV-vis (cyclohexane) λ_{max} (log ε): 207 (5.12), 243 (4.78), 294 (4.58), 307

(4.56), 391 (4.66). Anal. Calcd for C₁₀₄H₁₅₄O₈: C, 81.52; H, 10.13. Found: C, 81.57; H, 10.09.

1,3,6,8-Tetrakis(3,5-dioctyloxyphenyl)pyrene (4d). Mp (DSC) 81 °C; ¹H NMR δ 0.87 (t, *J* = 6.7 Hz, 24H), 1.26-1.52 (m, 80H), 1.80 (quintet, *J* = 6.9 Hz, 16H), 4.00 (t, *J* = 6.5 Hz, 16H), 6.56 (t, *J* = 2.2 Hz, 4H), 6.77 (d, *J* = 2.3 Hz, 8H), 8.00 (s, 2H), 8.22 (s, 4H); IR 1591 and 1175 (C-O-C) cm⁻¹. Anal. Calcd for C₁₀₄H₁₅₄O₈: C, 81.52; H, 10.13. Found: C, 81.45; H, 10.07.

Boronic esters 5. General procedure. *n*-BuLi (10 mmol, 2.5 M in hexane) was added dropwise to a stirred, cooled (-78 °C) solution of bromide **18** (10 mmol) in dry THF (30 mL) in an inert atmosphere. This solution was stirred for 1 hr followed by dropwise addition of a cooled (-78 °C) solution of (*i*-PrO)₃B (10 mmol) in dry THF (20 mL). The reaction mixture was warmed to rt overnight, followed by stirring with 10 % HCl. The product was extracted into Et₂O, the organic layer was separated, dried (Na₂SO)₄, and the solvent was evaporated to yield a white solid of the boronic acid⁹ The boronic acid (9 mmol) was dissolved in benzene (80 mL) along with ethylene glycol (9 mmol) and refluxed overnight with a Dean-Stark adapter. The solvent was evaporated to yield an off white solid (80%–95% yield). The analytical sample was obtained by recrystallization from hexanes.

4-Octyloxybenzeneboronic acid ethylene glycol ester (5b). Mp 51.5-52 °C; ¹H NMR δ 0.89 (t, *J* = 6.7 Hz, 3H), 1.29-1.48 (m, 10H), 1.79 (quintet, *J* = 6.7 Hz, 2H), 3.98 (t, *J* = 6.6 Hz, 2H), 4.35 (s, 4H), 6.90 (d, *J* = 8.6 Hz, 2H), 7.74 (d, *J* = 8.6 Hz, 2H); ¹³C NMR δ 14.1, 22.6, 26.0, 29.19, 29.22, 29.3, 31.8, 65.9, 67.8, 114.0, 136.5, 161.9 (the ¹³C-B signal was not located); IR 1248 (C-O-C) cm⁻¹; EI MS, *m/z* 276 (M, 7), 164 (100). Anal. Calcd for C₁₆H₂₅BO₃: C, 69.58; H, 9.12. Found: C, 69.51; H, 9.05.

3,4-Dioctyloxybenzeneboronic acid ethylene glycol ester (5c). Mp 37-39 °C; ¹H NMR δ 0.86-0.90 (m, 6H), 1.28-1.47 (m, 20H), 1.77-1.90 (m, 4H), 4.020 (t, *J* = 6.7 Hz, 2H), 4.017 (t, *J* = 6.6 Hz, 2H), 4.36 (s, 4H), 6.89 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 1.3 Hz, 1H) 7.39 (dd, *J*₁ = 8.0 Hz, *J*₂ = 1.4 Hz, 1H); ¹³C NMR δ 14.1, 22.7, 26.0, 29.19, 29.26, 29.33, 29.4, 31.8, 66.0, 68.8, 69.2, 112.7, 119.4, 128.7, 148.5, 152.1 (the ¹³C-B signal was not located); IR 1259 and 1142 (C-O-C) cm⁻¹; EI MS *m/z* 404 (M, 39), 180 (100). Anal. Calcd for C₂₄H₄₁BO₄: C, 71.28; H, 10.22. Found: C, 71.37; H, 10.31.

3,5-Dioctyloxybenzeneboronic acid ethylene glycol ester (5d). Mp 44-44.5 °C; ¹H NMR δ 0.89 (t, *J* = 6.7 Hz, 6H), 1.28-1.44 (m, 20H), 1.76 (quintet, *J* = 6.7 Hz, 4H), 3.95 (t, *J* = 6.6 Hz, 4H), 4.37 (s, 4H), 6.58 (t, *J* = 2.3 Hz, 1H), 6.93 (d, *J* = 2.4 Hz, 2H); ¹³C NMR δ 14.1, 22.7, 26.0, 29.27, 29.33, 31.8, 66.0, 68.0, 105.5, 112.3, 160.0 (the ¹³C-B signal was not located); IR 1166 (C-O-C) cm⁻¹; EI MS *m/z* 404 (M, 50), 180 (M-224, 100). Anal. Calcd for C₂₄H₄₁BO₄: C, 71.28; H, 10.22. Found: C, 71.38; H, 10.08.

4,4'-Dioctyloxybiphenyl (6b). Mp 116.5-117 °C (lit.¹⁰ mp 116-117 °C); ¹H NMR δ 0.90 (t, *J* = 6.7 Hz, 6H), 1.30-1.49 (m, 20H), 1.80 (quintet, *J* = 7.0 Hz, 4H), 3.99 (t, *J* = 6.6 Hz, 4H), 6.95 (d, *J* = 8.8 Hz, 4H), 7.46 (d, *J* = 8.8 Hz, 4H); ¹³C NMR δ 14.1, 22.7, 26.1, 29.25, 29.31, 29.37, 31.8, 68.1, 114.7, 127.6, 133.3, 158.2.

3,3',4,4'-Tetraoctyloxybiphenyl (6c). Mp 81-81.5 °C; ¹H NMR δ 0.89 (t, *J* = 6.2 Hz, 12H), 1.29-1.50 (m, 40H), 1.78-1.88 (m, 8H), 4.02 (t, *J* = 6.7 Hz, 4H), 4.05 (t, *J* = 6.7 Hz, 4H), 6.92 (d, *J* = 8.8 Hz, 2H), 7.03-7.07 (m, 4H). Anal Calcd. for C₄₄H₇₄O₄: C, 79.22; H, 11.18. Found: C, 79.39; H, 11.25.

3,3',5,5'-Tetraoctyloxybiphenyl (6d). Mp 51-52 °C; ¹H NMR δ 0.89 (t, *J* = 6.7 Hz, 12H), 1.26-1.46 (m, 40H), 1.79 (quintet, *J* = 7.0 Hz, 8H), 3.98 (t, *J* = 6.6 Hz, 8H), 6.44 (t, *J* = 2.2 Hz, 2H), 6.69 (d, *J* = 2.2 Hz, 4H). Anal Calcd. for C₄₄H₇₄O₄: C, 79.22; H, 11.18. Found: C, 79.08; H, 11.18.

3,3',5,5'-Tetrachloro-2,2',6,6'-tetranitrobiphenyl (7). Method A. A mixture of 1,3,5-trichloro-2,6-dinitrobenzene (**15**, 5.86 g, 21.6 mmol) and freshly prepared Cu (0.686 g, 10.8 mmol) in 5-*tert*-butyl-*m*-xylene (10 mL) was stirred under Ar at 150 °C. After 24 hrs the solvent was distilled off under reduced pressure. The crude product was dissolved in CH₂Cl₂ and adsorbed on silica gel, followed by purification on a short silica gel column with increasing polarity of hexane/CH₂Cl₂ mixture to yield 0.51 g of a yellow solid. The solid was recrystallized from an *i*-octane/toluene mixture to give 0.355 g (7% yield or 42% based on recovered starting material) of biphenyl **7**.

Method B. A mixture of 1-bromo-3,5-dichloro-2,6-dinitrobenzene¹¹ (**16**, 2.00 g, 6.33 mmol) and freshly prepared Cu (0.20 g, 3.17 mmol) in dry xylenes (10 mL) was stirred for 12 hrs at 130 °C under Ar. The reaction mixture was worked up as in Method A to give 0.485 g (33% yield, or 70% based on recovered starting material) of biphenyl **7** as a white solid: mp 268-270 °C; ¹H NMR δ 7.95 (s); ¹³C NMR δ 120.6, 130.9, 136.0,

146.4; IR 1567, 1549, and 1345 (NO₂) cm⁻¹. Anal Calcd. for C₁₂H₂Cl₄N₄O₈: C, 30.54; H, 0.43; N, 11.87. Found: C, 30.60; H, 0.51; N, 11.39.

Preparation of tetraaryltetranitrobiphenyls 8. General procedure. A mixture of tetrachloride **7** (1 mmol), boronic ester **5** (4.4 mmol), Pd(Ph₃P)₄ (0.2 mmol), 2M aqueous solution of Na₂CO₃ (4 mL), and DME was refluxed for 20 hrs under Ar. The product was isolated in 45%-75% yield as a yellow solid by column chromatography using a hexane/CH₂Cl₂ mixture with increasing polarity as an eluent, and followed by recrystallization from *i*-propanol.

3,3',5,5'-Tetrakis(4-octyloxyphenyl)-2,2',6,6'-tetranitrobiphenyl (8b). Mp 96-98 °C; ¹H NMR δ 0.89 (t, *J* = 6.7 Hz, 12H), 1.29-1.46 (m, 40H), 1.79 (quintet, *J* = 6.9 Hz, 8H), 3.98 (t, *J* = 6.5 Hz, 8H), 6.95 (d, *J* = 8.8 Hz, 8H), 7.31 (d, *J* = 8.7 Hz, 8H), 7.62 (s, 2H); IR 1181 and 1253 (C-O-C), 1353 and 1538 (NO₂) cm⁻¹. Anal Calcd. for C₆₈H₈₆N₄O₁₂: C, 70.93; H, 7.53; N, 4.87. Found: C, 71.13; H, 7.60; N, 4.87.

3,3',5,5'-Tetrakis(3,4-dioctyloxyphenyl)-2,2',6,6'-tetranitrobiphenyl (8c). Mp 86-91 °C; ¹H NMR δ 0.87 (t, *J* = 6.1 Hz, 12H), 0.89 (t, *J* = 6.0 Hz, 12H), 1.27-1.48 (m, 80H), 1.76-1.88 (m, 16H), 3.98 (t, *J* = 6.0 Hz, 8H), 4.02 (t, *J* = 6.5 Hz, 8H), 6.86-6.88 (m, 4H), 6.89-6.92 (m, 8H), 7.64 (s, 2H); IR 1142 and 1258 (C-O-C), 1353, 1516, and 1534 (NO₂) cm⁻¹. Anal Calcd. for C₁₀₀H₁₅₀N₄O₁₆: C, 72.17; H, 9.08; N, 3.37. Found: C, 72.43; H, 9.19; N, 3.36.

3,3',5,5'-Tetrakis(3,5-dioctyloxyphenyl)-2,2',6,6'-tetranitrobiphenyl (8d). ¹H NMR δ 0.88 (t, *J* = 6.7 Hz, 24H), 1.28-1.44 (m, 80H), 1.76 (quintet, *J* = 6.9 Hz, 16H), 3.92 (t, *J* = 6.5 Hz, 16H), 6.46 (d, *J* = 2.1 Hz, 8H), 6.51 (t, *J* = 2.1 Hz, 4H), 7.68 (s, 2H); IR 1171 (C-O-C), 1355, 1543, and 1585 (NO₂) cm⁻¹. Anal Calcd. for C₁₀₀H₁₅₀N₄O₁₆: C, 72.17; H, 9.08; N, 3.37. Found: C, 72.36; H, 9.08; N, 3.30.

2,2',6,6'-Tetranitrobiphenyl (12).¹² A mixture of 2,6-dinitrochlorobenzene (8.1 g, 0.04 mol), activated Cu (4.0 g, 0.063 mol), and dry xylene (30 mL) was stirred at 130 °C under Ar for 24 hrs. The reaction mixture was cooled to rt and passed through a silica gel plug with hexanes to remove xylenes. The product was eluted with CH₂Cl₂, and purified by using a short silica gel column (hexane/CH₂Cl₂, 2:1 followed by 1:1) followed by recrystallization (EtOH) to give 5.34 g (80% yield) of biphenyl **12** as yellow crystals: mp 215.5-216 °C (lit.^{7,12} mp 217-218 °C).

2,2',6,6'-Tetraaminobiphenyl (13).¹³ A mixture of tetranitrobiphenyl **12** (2.00 g, 6.0 mmol) in PtO₂ (0.14 g, 0.6 mmol) in EtOH (200 mL) was pressurized to 60 psi with H₂ in a hydrogenation bottle, and heated with a 275 W sun lamp. After 4 hrs the resulting red solution was cooled, the catalyst was filtered off, and the solvent was evaporated to give 1.27 g (90% yield) of tetraamine **13** as a red solid: ¹H NMR δ 3.69 (bs, 8H), 6.25 (d, *J* = 7.9 Hz, 4H), 7.00 (t, *J* = 7.9 Hz, 2H); EI MS *m/z* 214 (M, 100), 198 (67).

2,2',6,6'-Tetraamino-3,3',5,5'-tetrabromobiphenyl (14). Tetraamine **13** (1.11 g, 5.18 mmol) was suspended in AcOH. Concd. HCl (2 mL) was added followed by dropwise addition of Br₂ (1.1 mL). The reaction mixture was stirred overnight at rt. The resulting suspension was poured into dil. aq. solution of Na₂SO₃. The resulting light brown precipitate of the product was filtered. The crude product was dissolved in CH₂Cl₂, dried (Na₂SO₄) and passed through a silica gel plug with CH₂Cl₂ as an eluent. The solvent was evaporated to give 1.77 g (65% yield) of a brown solid. The analytical sample was recrystallized from hexane/toluene mixture: mp dec >250 °C; ¹H NMR δ 4.02 (s, 8H), 7.54 (s, 2H); EI-MS *m/z* 526, 528, 530, 532, 534 (M, 20:72:100:67:17). Anal. Calcd for C₁₂H₁₀Br₄N₄: C, 27.20; H, 1.90; N, 10.57. Found: C, 27.94; H, 1.88; N, 10.50.

5-Bromopyrocatechol (17c).¹⁴ Following a literature procedure, H₂O₂ (30%, 17 mL, 0.158 mol) was added slowly to the solution of 5-bromosalicylaldehyde (30.2 g, 0.150 mol) in aqueous NaOH (6.3 g, 0.158 mol). The reaction mixture became dark orange and hot. It was cooled to rt and acidified with conc. H₂SO₄, followed by the addition of NaHCO₃. The product was extracted with Et₂O, the organic layer was separated, and dried (Na₂SO₄). The solvent was evaporated and the product was isolated by short-path distillation (140 °C/0.3 Torr) as a pale yellow solid (26.14 g, 92% yield): mp 81-83 °C (lit.¹⁴ mp 86 °C); ¹H NMR δ 5.17 (s, 1H), 5.32 (s, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.93 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.3 Hz, 1H), 7.03 (d, *J* = 2.2 Hz, 1H).

Octyloxybromobenzenes 18. General procedure.¹⁵ A mixture of bromophenol **17** (0.1 mol), *n*-C₈H₁₇Br (0.1 mol), K₂CO₃ (0.3 mol), Adogen 464 (2 mL) in acetone (130 mL) was refluxed overnight. Inorganic solids were filtered off, and the solvent was evaporated. The product was isolated by short-path distillation.

4-Octyloxybromobenzene (18b).¹⁵ The product was obtained as a colorless oil in 90% yield: bp 130-140 °C/0.6 Torr; ¹H NMR δ 0.88 (t, *J* = 6.7 Hz, 3H), 1.28-1.45 (m,

10H), 1.76 (quintet, $J = 6.7$ Hz, 2H), 3.89 (t, $J = 6.6$ Hz, 2H), 6.76 (d, $J = 9.1$ Hz, 2H), 7.35 (d, $J = 8.8$ Hz, 2H); IR 1244 (C-O-C) cm^{-1} ; EI MS m/z 284 and 286 (M, 1:1), 172 and 174 (1:1).

3,4-Dioctyloxybromobenzene (18c).^{16,17} Mp 33-34 °C; ^1H NMR δ 0.88 (t, $J = 6.4$ Hz, 6H), 1.28-1.45 (m, 20H), 1.79 (quintet, $J = 6.5$ Hz, 4H), 1.81 (quintet, $J = 6.6$ Hz, 2H) 3.948 (t, $J = 6.6$ Hz, 2H), 3.954 (t, $J = 6.6$ Hz, 2H), 6.73 (d, $J = 9.2$ Hz, 1H), 6.95-7.00 (m, 2H); ^{13}C NMR δ 14.1, 22.65, 22.72, 26.0, 29.15, 29.25, 29.32, 29.34, 31.8, 31.9, 69.4, 69.6, 112.8, 115.2, 117.0, 123.4, 148.4, 150.1; EI MS m/z 412 and 414 (M, 18:20), 188 and 190 (100:98). Anal. Calcd for $\text{C}_{22}\text{H}_{37}\text{BrO}_2$: C, 63.91; H, 9.02; Br, 19.33. Found: C, 63.86; H, 9.05; Br, 19.40.

3,5-Dioctyloxybromobenzene (18d). A mixture of 3,5-dioctyloxybenzoic acid **20** (1.28 g, 3.4 mmol) and SOCl_2 (2 mL) was gently refluxed for 2 hrs. Excess SOCl_2 was removed under reduced pressure and the resulting acid chloride was distilled (190 °C / 0.2 Torr) and used without further purification. The acid chloride and AIBN (11 mg, 0.07 mmol) were dissolved in CBrCl_3 (5 mL). 2-Mercaptopyridine N-oxide, sodium salt was dissolved in CBrCl_3 and heated to reflux. The acid chloride/AIBN solution was added dropwise over 45 min., then refluxed for another 15 min. until the yellow color disappeared. CBrCl_3 was distilled and recovered. The resulting brown oil was passed through a silica gel plug using toluene as an eluent. The pyridine side product was distilled off (100 °C / 0.2 Torr) and the residue was passed through a silica gel plug with hexane as an eluent to yield 0.70 g (50% yield) of 3,5-dioctyloxybromobenzene (**18d**) as a pale yellow oil: bp 190-210°C/0.4 Torr; ^1H NMR δ 0.89 (t, $J = 6.4$ Hz, 6H), 1.29-1.43 (m, 20H), 1.75 (quintet, $J = 6.5$ Hz, 4H), 3.89 (t, $J = 6.5$ Hz, 4H), 6.36 (t, $J = 1.9$ Hz, 1H), 6.63 (d, $J = 2.1$ Hz, 2H); ^{13}C NMR δ 14.1, 22.6, 26.0, 29.1, 29.2, 29.3, 31.8, 68.2, 100.5, 110.2, 122.8, 160.7; IR 1167 (C-O-C), 1575 and 1598 cm^{-1} ; EI MS m/z 412, 414 (M, 9:8), 188, 190 (100:98). Anal. Calcd for $\text{C}_{22}\text{H}_{37}\text{BrO}_2$: C, 63.91; H, 9.02; Br, 19.33. Found: C, 64.16; H, 8.91; Br, 19.21.

3,5-Dioctyloxybenzoic acid (20).¹⁸ A mixture of methyl 3,5-dihydroxybenzoate (10.25 g, 0.061 mol, obtained by esterification of 3,5-dihydroxybenzoic acid with MeOH in the presence of catalytic amounts of H_2SO_4), $n\text{-C}_8\text{H}_{17}\text{Br}$ (22 mL, 0.128 mol), K_2CO_3 (55.0 g, 0.4 mol), Adogen 464 (0.02 mL), and acetone (400 mL) was stirred and refluxed

overnight. The reaction mixture was cooled and inorganic solids were filtered off. The solvent was evaporated and the resulting yellowish oily product, solidified upon standing. Methyl 3,5-dioctyloxybenzoate was recrystallized from hexane to give 23.09 g (96% yield) of white crystals: mp 42-42.5 °C (lit.¹⁹ mp 41 °C); ¹H NMR δ 0.89 (t, *J* = 6.7, 6H), 1.29-1.45 (m, 20H), 1.78 (quintet, *J* = 7.4, 4H), 3.90 (s, 3H), 3.97 (t, *J* = 6.5, 4H), 6.63 (t, *J* = 2.3, 1H), 7.16 (d, *J* = 2.3, 2H).

Methyl 3,5-dioctyloxybenzoate (22.30 g, 0.057 mol) was added to a solution of NaOH (2.73 g, 0.068 mol) in MeOH (200 mL) and the mixture was refluxed until no more starting material was detected by TLC. The reaction mixture was cooled, poured into water, and acidified with HCl. The product was extracted with Et₂O, dried (Na₂SO₄) and the solvent was evaporated to yield a white solid. The product was recrystallized from hexanes to give 18.4 g (86% yield) of acid **20** as white crystals: mp 58.5-59.5 °C; ¹H NMR δ 0.89 (t, *J* = 6.4 Hz, 6H), 1.29-1.45 (m, 20H), 1.76 (quintet, *J* = 7.8 Hz, 4H), 3.98 (t, *J* = 6.6 Hz, 4H), 6.68 (t, *J* = 2.2 Hz, 1H), 7.21 (d, *J* = 2.2 Hz, 2H); ¹³C NMR δ 14.1, 22.7, 26.0, 29.1, 29.2, 29.3, 31.8, 68.3, 107.5, 108.1, 130.8, 160.2, 172.4; IR 3100-2500 (O-H), 1697 (C=O), 1173 and 1063 (C-O-C) cm⁻¹. Anal. Calcd for C₂₃H₃₈O₄: C, 72.98; H, 10.12. Found: C, 72.90; H 10.21.

8. Archive data for MP2/6-31G(d) optimizations of 21a–21c.

Conformational GS and TS for phenyl derivatives **21** were optimized at the MP2/6-31G(d) level of theory using B3LYP/6-31G(d) geometry and force constants as the starting points.

8-Phenylcinnoline GS (**21a-GS**)

```
1\1\GINC-MONSTER\FOpt\RMP2-FC\6-31G(d)\C14H10N2\PIOTR\29-Sep-2006\0\#\#
P MP2/6-31G* FOPT GEOM(NOANGLE, NODISTANCE) FCHECK\8-Ph-cinnoline, st
arting at B3LYP/6-31G* geom, C1 symm\0,1\C, -0.025471105, 1.0694481045,
-0.1623750621\C, 0.025234775, 2.3987441238, 0.3639449007\C, -0.0996642315,
3.4390200871, -0.5757731391\C, -0.2698521238, 3.0986520356, -1.9014151398\
N, -0.3322540114, 1.8140650178, -2.3541521046\N, -0.2139660021, 0.811217051
7, -1.4948000664\C, 0.1898416716, 2.605005177, 1.755570905\C, 0.2942896881,
1.5141882092, 2.5913999451\C, 0.2522488066, 0.1994031907, 2.0736139825\C, 0
.0959849108, -0.0540358608, 0.7177009801\C, 0.0428230324, -1.4474408791, 0.
2303950192\C, 0.8309761303, -1.882363861, -0.8472329166\C, 0.7999182423, -3
.218771875, -1.2421908778\C, -0.0144377415, -4.1369329073, -0.5734729025\C
, -0.8046398383, -3.7103019258, 0.4953600334\C, -0.7740379507, -2.374526911
6, 0.8970429946\H, -0.3727821221, 3.8509700053, -2.6790221694\H, -0.0678533
193, 4.4809400987, -0.2620541689\H, -1.4091130254, -2.0361569278, 1.7136399
432\H, -1.4503438262, -4.4157019518, 1.0133860131\H, -0.0383106538, -5.1771
```

Supplementary material (ESI) for Journal of Materials Chemistry
This journal is © The Royal Society of Chemistry 2007

899185,-0.8893848723\H,1.4162043175,-3.5459638606,-2.076338828\H,1.460
5061184,-1.1718838363,-1.3733118975\H,0.3696238172,-0.642858781,2.7523
040158\H,0.4256316094,1.6603082504,3.6612839491\H,0.2306915806,3.62004
21915,2.1467508767\Version=x86-Linux-G98RevA.9\HF=-644.8388768\MP2=-6
46.9411922\RMSD=8.871e-09\RMSF=1.372e-06\Dipole=1.3296974,0.2367548,0.
7668372\PG=C01 [X(C14H10N2)]\@

8-Phenylcinnoline TS (21a-TS)

1\1\GINC-MONSTER\FTS\RMP2-FC\6-31G(d)\C14H10N2\PIOTR\24-Apr-2004\0\#P
MP2/6-31G* FOPT(RCFC, TIGHT, TS) GEOM(NOANGLE, NODISTANCE, CHECK) #P
FCHECK GUESS=CHECK\8-Ph-cinnoline TS starting at B3LYP/6-31G* geom Cs
symmetry\0,1\C,0.5819770374,0.,0.9498697697\C,0.5555082593,0.,2.3867
704737\C,1.7986432428,0.,3.0452529448\C,2.9454504401,0.,2.2831167285\N
,2.9349056673,0.,0.9232806787\N,1.7762055078,0.,0.2800290031\C,-0.6681
885705,0.,3.0932871526\C,-1.8374162998,0.,2.3721233547\C,-1.8174835822
,0.,0.9620155409\C,-0.6537001043,0.,0.1921066711\C,-0.7615015469,0.,-1
.3034509735\C,0.3532985595,0.,-2.1700290934\C,0.1941981131,0.,-3.55655
1442\C,-1.0713483023,0.,-4.1381886834\C,-2.1872035444,0.,-3.3013479773
\C,-2.0352367559,0.,-1.917112847\H,3.9377004297,0.,2.7263487864\H,1.84
41325883,0.,4.1328533102\H,-2.9469762036,0.,-1.3311527441\H,-3.1894256
453,0.,-3.7240867225\H,-1.1884546246,0.,-5.219293255\H,1.0828037504,0.,
-4.1839068628\H,1.3492957032,0.,-1.7530931423\H,-2.7854665386,0.,0.47
72430379\H,-2.7976878403,0.,2.8831085714\H,-0.66568152,0.,4.1816415321
\Version=x86-Linux-G98RevA.9\State=1-A'\HF=-644.829176\MP2=-646.93083
59\RMSD=5.470e-09\RMSF=4.312e-06\Dipole=-0.9541288,0.,1.2504045\PG=CS
[SG(C14H10N2)]\@

1-Phenyl naphthalene GS (21b-GS)

1\1\GINC-MONSTER\FOpt\RMP2-FC\6-31G(d)\C16H12\PIOTR\25-Apr-2004\0\#P
MP2/6-31G* FOPT(RCFC, TIGHT) GEOM(NOANGLE, NODISTANCE) FCHECK\1-Ph-na
phthalene, starting at B3LYP/6-31G* geom, C1 symm\0,1\C,0.1859322461,
-1.0215081879,0.1480227414\C,0.4940348318,-2.3134790215,-0.3959980558\
C,0.5777220338,-3.4298458324,0.4761296824\C,0.4221620644,-3.2776557731
,1.8376380533\C,0.1617304249,-1.9987353853,2.3792220757\C,0.0599957754
,-0.8938642728,1.5578380124\C,0.6817988731,-2.4585127271,-1.7939115365
\C,0.61406236,-1.3611272297,-2.626323331\C,0.3091030605,-0.0891266062,
-2.0987307389\C,0.0922788163,0.0965364424,-0.7402828151\C,-0.251236606
3,1.4492272347,-0.2469253517\C,0.6118359722,2.5279239285,-0.4930423411
\C,0.2783730859,3.8148378162,-0.0678027658\C,-0.9218131565,4.040487723
4,0.609873264\C,-1.7890960844,2.9730410268,0.8572174531\C,-1.457643144
4,1.6861069555,0.432353251\H,-0.1215812464,0.0865413074,1.9891649365\H
,0.0639221692,-1.8796296249,3.4560698515\H,0.4941183154,-4.1408738541,
2.4953840975\H,0.7965210456,-4.4092815344,0.0527866085\H,-2.142472896,
0.8585508653,0.6065428067\H,-2.7298461967,3.1448930463,1.3754886757\H,
-1.1813103907,5.0427880615,0.9421782999\H,0.9588895563,4.6411715901,-
.2604939031\H,1.552941022,2.3464534557,-1.0086671674\H,0.2217387737,0.
7660439577,-2.7666524487\H,0.7658991035,-1.4769646412,-3.697254263\H,0.
9057374267,-3.4455291779,-2.1962130785\Version=x86-Linux-G98RevA.9\H
F=-612.8970686\MP2=-614.9260051\RMSD=4.905e-09\RMSF=1.425e-06\Dipole=-
0.0156215,0.0534671,0.0218567\PG=C01 [X(C16H12)]\@

1-Phenyl naphthalene TS (21b-TS)

1\1\GINC-MONSTER\FTS\RMP2-FC\6-31G(d)\C16H12\PIOTR\25-Apr-2004\0\#P M
P2/6-31G* FOPT(RCFC, TIGHT, TS) GEOM(NOANGLE, NODISTANCE, CHECK) #P FC
HECK GUESS=CHECK\1-Ph naphthalene TS starting at B3LYP/6-31G* geom Cs
symmetry\0,1\C,-0.1916864259,-0.2291993124,1.0693868735\C,0.29283808
75,0.1527501429,2.3740741915\C,-0.5543224993,0.0563229414,3.5092316206
\C,-1.8203198038,-0.4764848716,3.4160392901\C,-2.2502414267,-0.9898009

```
544,2.1767333804\C,-1.4619803849,-0.873446294,1.0472757761\C,1.6379302
255,0.5551380245,2.5542862254\C,2.4982892107,0.5360489018,1.4822768434
\C,2.0069233728,0.2631195645,0.193535883\C,0.6620073032,-0.0023863946,
-0.0798546191\C,0.2276299011,0.0541739912,-1.5157808576\C,1.1096424563
,0.6071136328,-2.4752608745\C,0.7943591617,0.6784140853,-3.8297296674\C,
-0.4428858774,0.2347809487,-4.295335501\C,-1.3609392487,-0.246741965
8,-3.3661686673\C,-1.0377379094,-0.3271343631,-2.0102590744\H,-1.79556
71533,-1.3885928557,0.1599481997\H,-3.2039832444,-1.5080345835,2.10541
62398\H,-2.4563467698,-0.5507539758,4.294807016\H,-0.1652366814,0.3889
865899,4.4705083021\H,-1.8222670092,-0.6553217262,-1.3503326149\H,-2.3
505890611,-0.5630968014,-3.6881359852\H,-0.6950321703,0.2914592288,-5.
3513071138\H,1.51735009,1.1089207512,-4.5189891229\H,2.0552971435,1.03
75159448,-2.1692143748\H,2.7241772482,0.286788692,-0.6183443697\H,3.55
37184798,0.7641252718,1.6132633229\H,1.9814422722,0.8319950017,3.54967
5564\\Version=x86-Linux-G98RevA.9\HF=-612.8707554\MP2=-614.9020174\RMS
D=9.110e-09\RMSF=1.537e-06\Dipole=0.0271466,0.0156375,0.0538366\PG=C01
[X(C16H12)]\ \@
```

Biphenyl GS (21c-GS)

```
1\1\GINC-MONSTER\FOpt\RMP2-FC\6-31G(d)\C12H10\PIOTR\22-Apr-2004\0\#P
MP2/6-31G* FOPT(RCFC, TIGHT) GEOM(NOANGLE, NODISTANCE) FCHECK\Bipheny
l starting at B3LYP/6-31G* geom D2 symmetry\0,1\C,0.0507183233,-1.591
8702728,-1.0179803649\C,-1.4183758052,0.3171454448,-1.2085264496\C,1.7
494267486,0.3209990358,0.6398226376\C,-0.3817692667,0.9537257922,1.586
684177\C,2.4051337186,0.9307643847,1.7095817921\C,0.2750138129,1.56726
64794,2.6536208533\C,-0.6043427684,-2.2020916006,-2.0878751996\C,-2.07
58047631,-0.2959392636,-2.2753274459\C,1.6703166165,1.5568182019,2.719
2271299\C,-1.6703166165,-1.5568182019,-2.7192271299\C,0.3475783278,0.3
239602971,0.5658474624\C,-0.3475783278,-0.3239602971,-0.5658474624\H,0
.861437999,-2.109351958,-0.5089679384\H,-1.7170101434,1.311916146,-0.8
838787613\H,2.3248926227,-0.1401422643,-0.1603867517\H,-1.4693204783,0
.9375780763,1.5532334513\H,3.4920537573,0.926854705,1.7497239569\H,-0.
3035527679,2.0449868776,3.4410634114\H,-0.2893586167,-3.1879019942,-2.
4225163528\H,-2.8991423727,0.2160604116,-2.7682710155\H,2.181812477,2.
0335577961,3.5519275934\H,-2.181812477,-2.0335577961,-3.5519275934\\Ve
rsion=x86-Linux-G98RevA.9\State=1-A\HF=-460.2511491\MP2=-461.76918\RMS
D=5.847e-09\RMSF=2.263e-07\Dipole=0.,0.,0.\PG=D02 [C2(H1C1C1.C1C1H1),X
(C8H8)]\ \@
```

Biphenyl TS (21c-TS)

```
1\1\GINC-MONSTER\FTS\RMP2-FC\6-31G(d)\C12H10\PIOTR\22-Apr-2004\0\#P M
P2/6-31G* FOPT(RCFC, TIGHT, TS) GEOM(NOANGLE, NODISTANCE, CHECK) #P FC
HECK GUESS=CHECK\Biphenyl TS starting at B3LYP/6-31G* geom D2h symmet
ry\0,1\C,-1.4813022579,0.,-1.1999464957\C,-1.4813020989,0.,1.19994669
2\C,1.4813020989,0.,-1.199946692\C,1.4813022579,0.,1.1999464957\C,2.87
5553185,0.,-1.2010672783\C,2.8755533441,0.,1.2010668974\C,-2.875553344
1,0.,-1.2010668974\C,-2.875553185,0.,1.2010672783\C,3.5849676658,0.,-0
.0000002375\C,-3.5849676658,0.,0.0000002375\C,0.7453481875,0.,-0.00000
00494\C,-0.7453481875,0.,0.0000000494\H,-0.9746706051,0.,-2.1594935792
\H,-0.974670319,0.,2.1594937083\H,0.974670319,0.,-2.1594937083\H,0.974
6706051,0.,2.1594935792\H,3.4078176652,0.,-2.1496022634\H,3.4078179499
,0.,2.149601812\H,-3.4078179499,0.,-2.149601812\H,-3.4078176652,0.,2.1
496022634\H,4.6721654129,0.,-0.0000003095\H,-4.6721654129,0.,0.0000003
095\\Version=x86-Linux-G98RevA.9\State=1-AG\HF=-460.2458949\MP2=-461.7
628653\RMSD=6.800e-09\RMSF=1.198e-06\Dipole=0.,0.,0.\PG=D02H [C2(H1C1
C1.C1C1H1),SG(C8H8)]\ \@
```

9. References

- (1) In part described in M. J. Sienkowska, *Dissertation*, Vanderbilt University 2004. J. M. Farrar, *Dissertation*, Vanderbilt University 2001.
- (2) R. J. Bushby; O. R. Lozman; L. A. Mason; N. Taylor; S. Kumar *Mol. Cryst. Liq. Cryst.* 2004, **410**, 171-181.
- (3) N. Miyaura; T. Yanagi; A. Suzuki *Synth. Commun.* 1981, **11**, 513-519.
- (4) J. F. Corbett; P. F. Holt *J. Chem. Soc.* 1961, 3695-3699.
- (5) J. M. Farrar; M. Sienkowska; P. Kaszynski *Synth. Commun.* 2000, **30**, 4039-4045.
- (6) K. Ogino; S. Iwashima; H. Inokuchi; Y. Harada *Bull. Chem. Soc. Jpn.* 1965, **38**, 473-477.
- (7) H. Stetter; M. Schwarz *Chem. Ber.* 1957, **90**, 1349-1351.
- (8) J. M. Farrar, *Dissertation*, Vanderbilt University 2001.
- (9) 4-Octyloxyphenylboronic acid and 3,4-dioctyloxyphenylboronic acid are known: T. Yatabe, M. A. Harbison, J. D. Brand, M. Wagner, K. Müllen, P. Samori, J. P. Rabe, *J. Mater. Chem.* 2000, **10**, 1519-1525; S. J. Lock, J. W. Goodby, M. Hird, K. J. Toyne, *J. Mater. Chem.* 1995, **5**, 2175-2182; M. C. Artal, K. J. Toyne, J. W. Goodby, J. Barberá, D. J. Photinos, *J. Mater. Chem.* 2001, **11**, 2801-2807.
- (10) L. Ebersson; B. Helgée *Acta Chem. Scand., Ser. B* 1977, **31**, 813-817.
- (11) J. T. Manka; F. Guo; J. Huang; H. Yin; J. M. Farrar; M. Sienkowska; V. Benin; P. Kaszynski *J. Org. Chem.* 2003, **68**, 9574-9588.
- (12) W. Borsche; D. Rantscheff *Ann.* 1911, **379**, 152-182.
- (13) P. F. Holt; R. Oakland *J. Chem. Soc.* 1964, 6090-6094.
- (14) H. D. Dakin *Am. Chem. J.* 1909, **42**, 477-487.
- (15) G. W. Gray; M. Hird; D. Lacey; K. J. Toyne *J. Chem. Soc., Perkin Trans. 2* 1989, 2041-2053.
- (16) J. W. Goodby; M. Hird; K. J. Toyne; T. Watson *J. Chem. Soc. Chem. Commun.* 1994, 1701-1702.
- (17) M. C. Artal; K. J. Toyne; J. W. Goodby; J. Barberá; D. J. Photinos *J. Mater. Chem.* 2001, **11**, 2801-2807.
- (18) G. Pickaert; R. Ziessel *Synthesis* 2004, 2716-2726.
- (19) P. B. Rheiner; D. Seebach *Chem. Eur. J.* 1999, **5**, 3221-3236.