

# A Simple Multichromophore Design for Energy Transfer in Distyrylbenzenes with Pyrene Pendants

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**Figure S1.** Qualitative overlap of pyrene emission spectrum and core (**11**) absorption spectrum p S1

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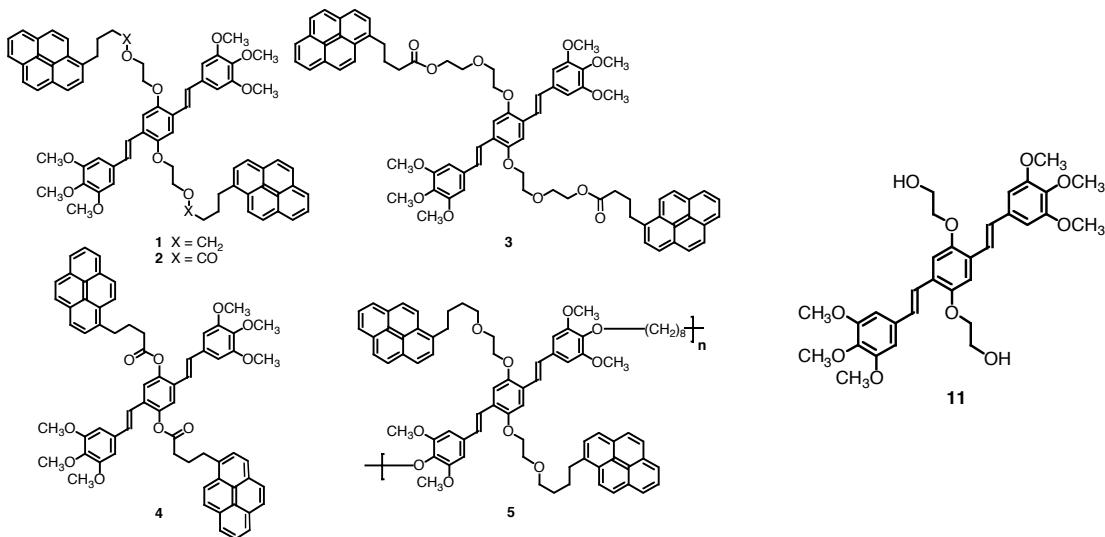
**Figure S4.** Solvent effect on luminescence of physical mixtures of pyrene with **11**. p S4

**Figure S5.** Solvent effect on luminescence of model compound **19**. p S4

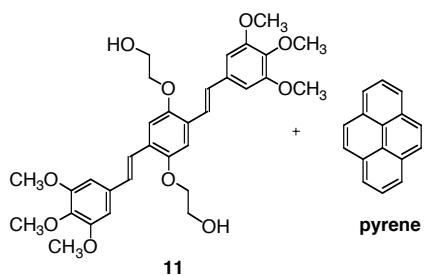
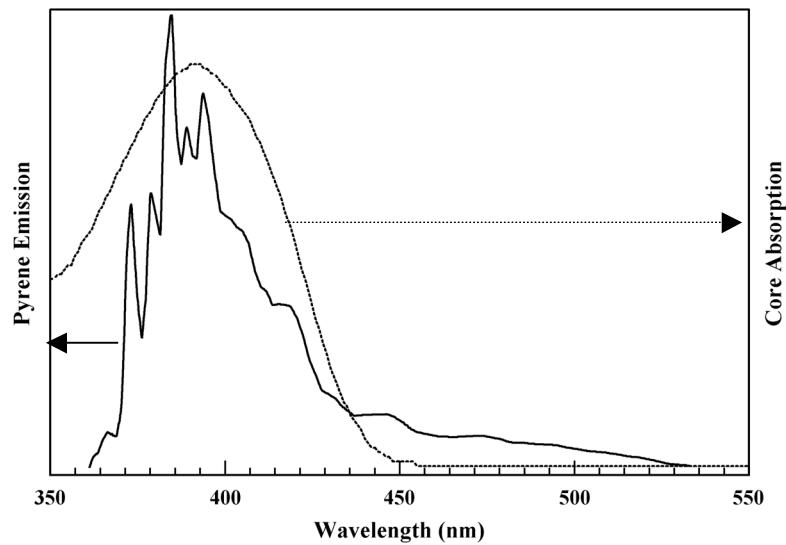
**Figure S6.** Molecular mechanics optimized structure of **1**. p S5

**Figure S7.** 2D NOESY spectrum of **1** in  $\text{CDCl}_3$  with a D8 time of 500 ms. p S6

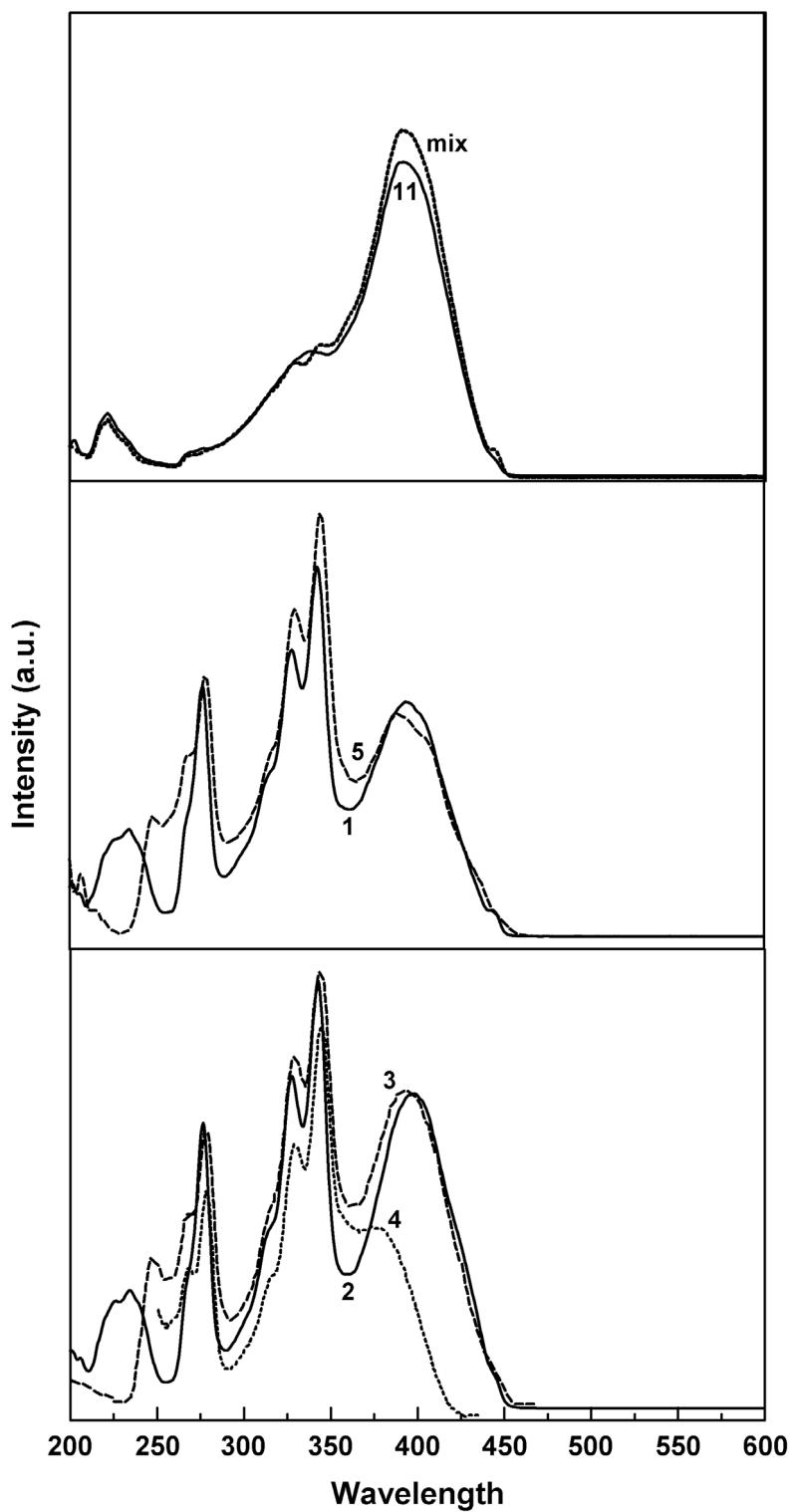
**Synthetic details.** p S7



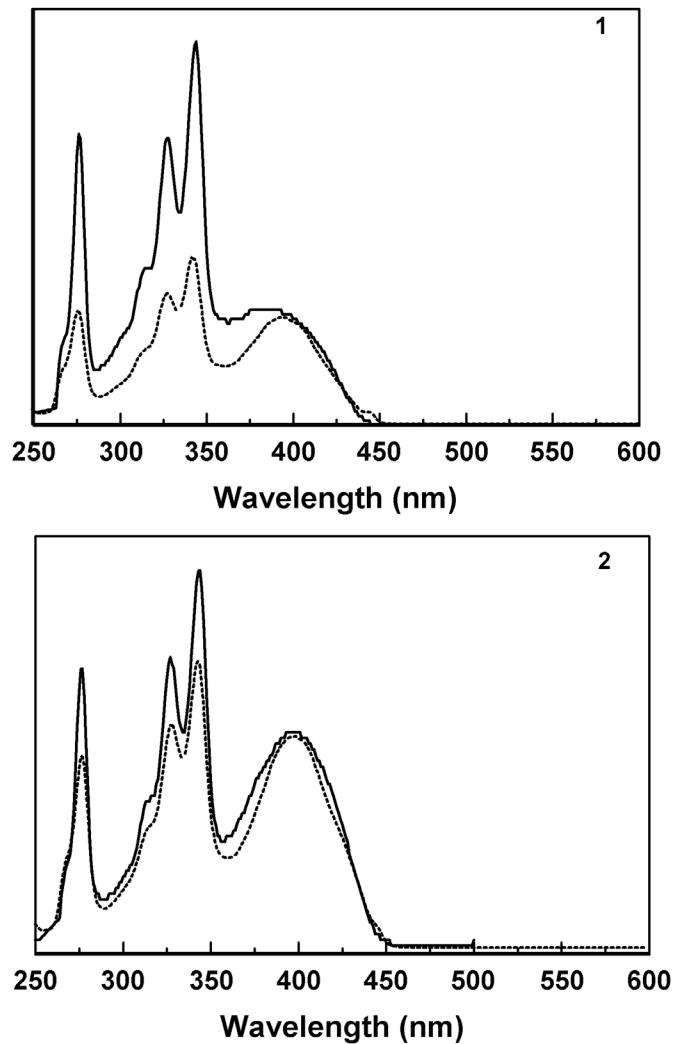
**Figure S1.** Qualitative overlap of pyrene emission spectrum and core (**11**) absorption spectrum shows good overlap of pyrene emission with core absorption.



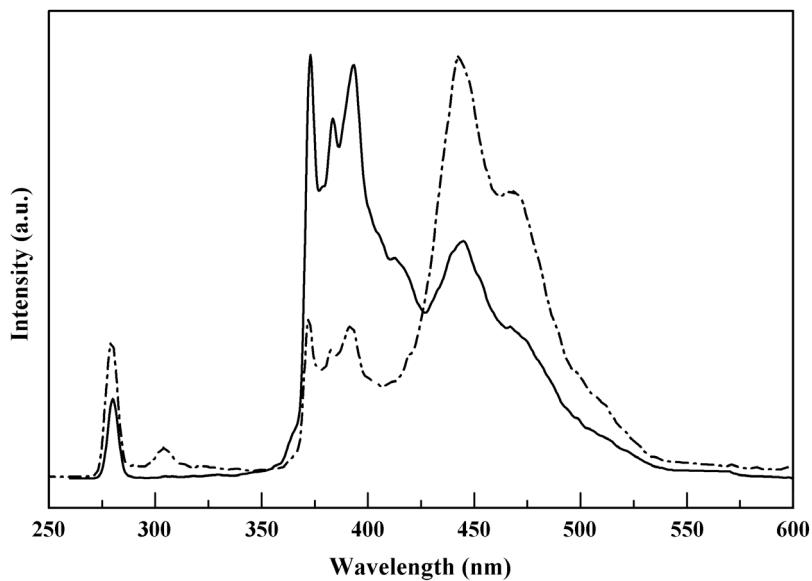
**Figure S2.** Excitation spectra for **11**, 1:2 mixture of **11** with pyrene, and **1-5**. All spectra in chloroform at room temperature at about 1 micromolar concentrations, all spectra monitored at 445 nm (core component emission tail).



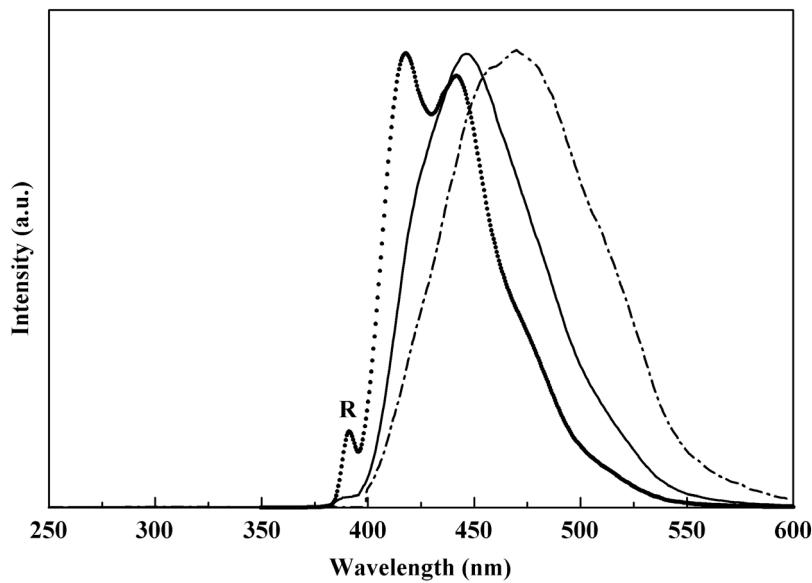
**Figure S3.** Example comparisons of UV-vis (solid lines) and excitation spectra (dashed lines) in chloroform for **1** and **2**, normalized on the maxima of the long wavelength peaks at about 400 nm. Excitation spectra monitored at 445 nm. The normalized ratio  $\text{Area}(\text{excit})/\text{Area}(\text{UV}) = \eta_{\text{ET}}$ , the energy transfer efficiency.



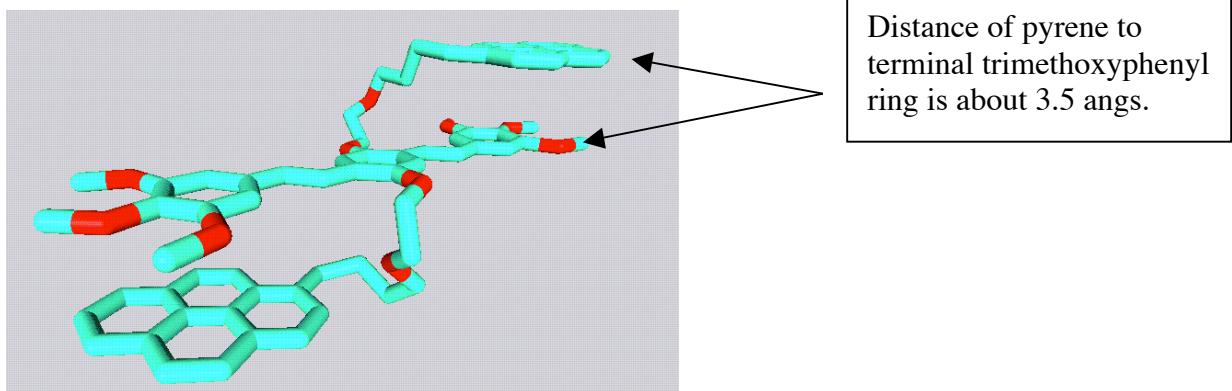
**Figure S4.** Solvent effect on luminescence of physical mixtures of pyrene with **11**. Solid line in chloroform, broken line in tetrahydrofuran; both spectra obtained with 276 nm excitation. Ordinate scales are normalized for the spectra relative to one another.



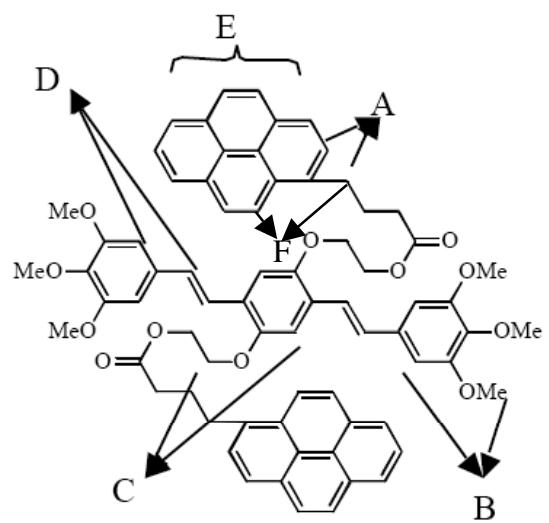
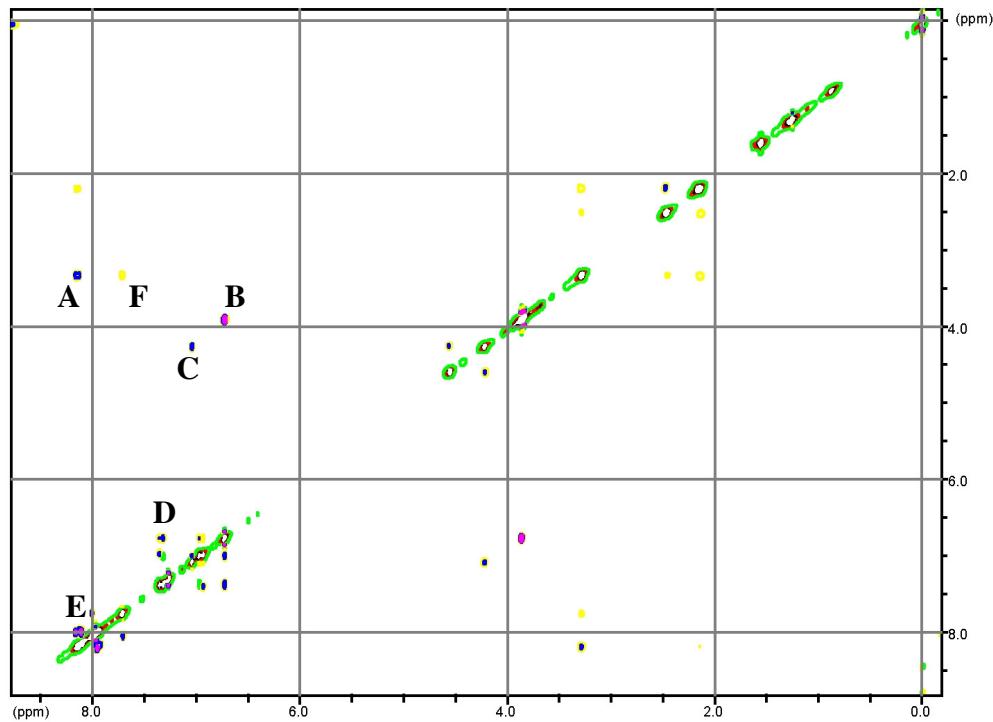
**Figure S5.** Solvent effect on luminescence of model compound **19**. Spectra obtained with 365 nm excitation. Ordinate scales are normalized for the spectra relative to one another.



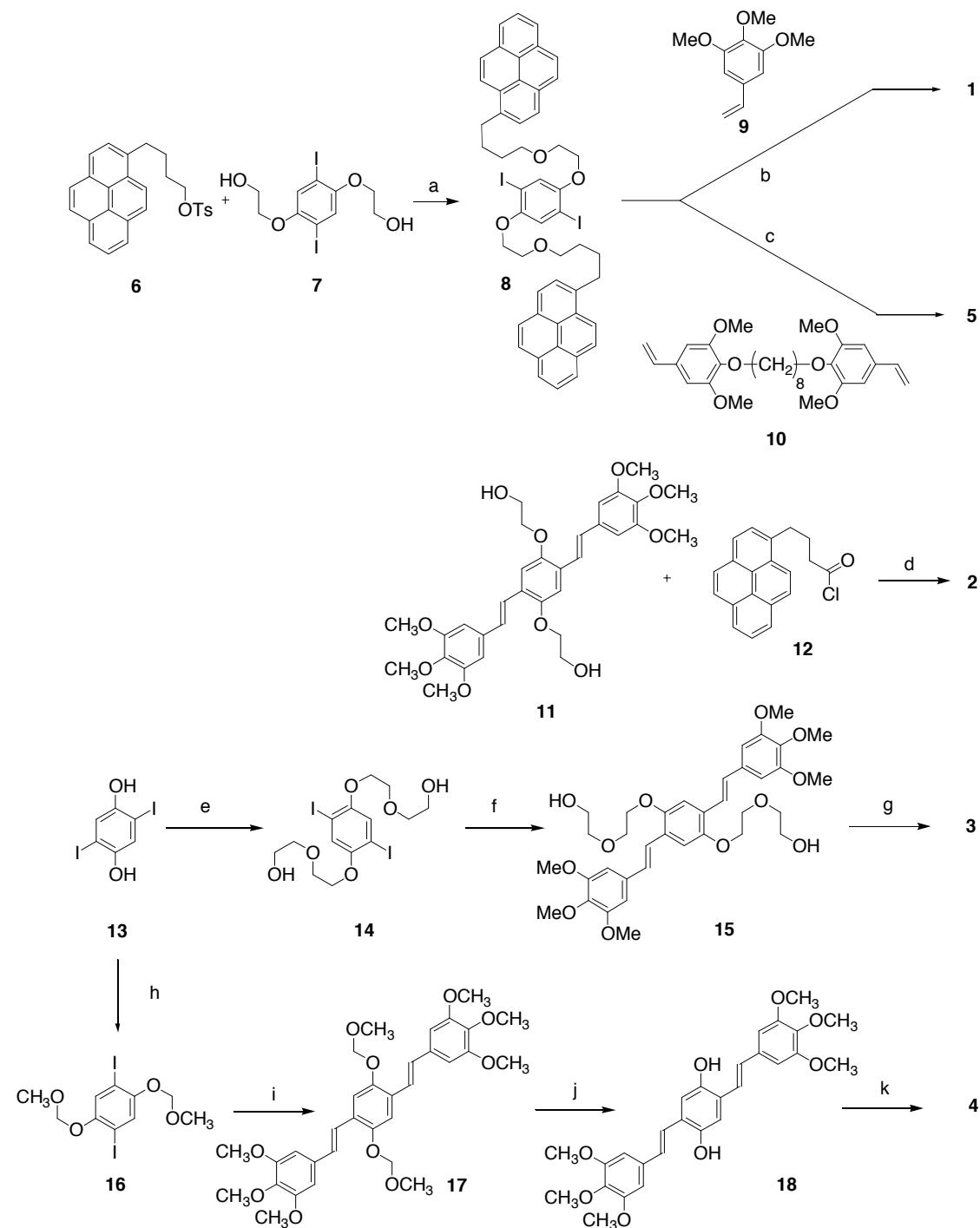
**Figure S6.** Molecular mechanics optimized structure of **1**. Computations were carried out using the UFF force field (Rappe, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A., III; Skiff, W.M. *J. Am. Chem. Soc.*, **1992**, *114*, 10024 within the Cerius<sup>2</sup> suite of programs by Accelrys (version 3.8 for SGI computer using Irix 6.5.x, (1998)).



**Figure S7.** 2D NOESY spectrum of **1** in  $\text{CDCl}_3$  with a D8 time of 500 ms..



### Synthetic Details.



**Scheme 1.** Multichromophore syntheses. (a) NaH, THF, heat 7 days, 28%. (b) Pd(OAc)<sub>2</sub>, P(*o*-tolyl)<sub>3</sub>, DMF/NBu<sub>3</sub>, 85–90 °C, 76%. (c) Pd(OAc)<sub>2</sub>, P(*o*-tolyl)<sub>3</sub>, DMF/NBu<sub>3</sub>, 120–125 °C, 40%. (d) NEt<sub>3</sub>, 24 h, 70%. (e) 2-butanone, K<sub>2</sub>CO<sub>3</sub>, 18-crown-6, heat 7 days, 61%. (f) Pd(OAc)<sub>2</sub>, P(*o*-tolyl)<sub>3</sub>, DMF/NBu<sub>3</sub>, 120 °C, 77%. (g) 12, CH<sub>2</sub>Cl<sub>2</sub>, NEt<sub>3</sub>/DMAP, 40%. (h) ClCH<sub>2</sub>OCH<sub>3</sub>, HN(*i*-Pr)<sub>2</sub>/CH<sub>2</sub>Cl<sub>2</sub>, 94%. (i) Pd(OAc)<sub>2</sub>, P(*o*-tolyl)<sub>3</sub>, DMF/NBu<sub>3</sub>, 105 °C, 91%. (j) *p*-toluenesulfonic acid, r.t., EtOH/CH<sub>2</sub>Cl<sub>2</sub>, 84%. (k) 4-(1-pyrenyl)butyric acid, PPh<sub>3</sub>/NEt<sub>3</sub>/CCl<sub>4</sub>, CH<sub>3</sub>CN, 48 h, 56%.

**General Methods.** All commercially available materials were used as received. Ether and THF were dried first over calcium hydride and then at reflux over sodium/benzophenone. Melting points are uncorrected. Molecular weights of polymers were measured by gel permeation chromatography in THF and referenced against linear polystyrene standards using a three-column system (Polymer Laboratories 300 × 7.5 mm, 2 mixed-D, 50 Å), a Knauer K-501 pump with a K-2301 refractive index detector and a K-2600 UV detector (395 nm). <sup>1</sup>H NMR and <sup>13</sup>C-NMR spectral peak positions are reported relative to the internal reference specified in each case. Mass spectrometry was obtained under high-resolution fast atom bombardment or electron impact ionization conditions at the University of Massachusetts at Amherst Mass Spectrometry and Molecular Weight Analysis Facility. Relative quantum yields ( $\phi_{FL}$ ) were measured using quinine sulfate in 0.10 M H<sub>2</sub>SO<sub>4</sub> as a standard ( $\phi_{FL} = 0.546$ ), according to the procedure of Chen et al. [Chen, Z.; Huang, W.; Wang, L.; Kang, E.; Chen, B.; Lee, C. S.; Lee, S. T. *Macromolecules* **2000**, *33*, 9015].

**4-(1-Pyrenyl)butyl tosylate (6).** This compound was made by a literature procedure: mp 95-97 °C (lit mp 91-92 °C[Winnik, F.; Winnik, M.; Tazuke, S.; Ober, C. *Macromolecules* **1987**, *20*, 38]). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 1.83 (m, 4 H), 2.34 (s, 3 H), 3.28 (t, 2 H, J= 6.5 Hz), 4.11 (t, 2 H, J= 6.5 Hz), 7.24, 7.80 (d, 4 H, J= 8 Hz), 8.0-8.22 (m, 9 H).

**2,5-Diiodo-1,4-hydroquinol (13).** This compound was made by a literature procedure: mp 197-199 °C (lit. mp 195-197 °C[Winnik, F.; Winnik, M.; Tazuke, S.; Ober, C. *Macromolecules* **1987**, *20*, 38]). <sup>1</sup>H-NMR (acetone-d<sub>6</sub>): δ 7.29 (s, 2 H), 8.82 (s, 2 H); <sup>13</sup>C-NMR (acetone-d<sub>6</sub>): δ 83.15, 123.65, 150.43.

**1,4-Bis(2-hydroxyethoxy)-2,5-diiodobenzene (7).** This compound was made from **13** by a previously published procedure[Sierra, C. A.; Lahti, P. M. *Chem. Mater.* **2004**, *16*, 55]: mp 169-170 °C. <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>): δ 3.67 (m, 4 H), 3.97 (t, 4 H, J= 5 Hz), 4.83 (t, 2 H, J= 5 Hz), 7.36 (s, 2 H); <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>): 60.55, 72.80, 88.00, 123.99, 153.60.

**2,5-Bis(2-[4-(1-pyrenyl)butoxy]ethoxy)-1,4-diiodobenzene (8).** Under an atmosphere of argon at room temperature, **7** (549 mg, 1.22 mmol) was added to a suspension of 95% dry sodium hydride (381 mg, 15.8 mmol) in 20 mL of dry THF. After 30 min of stirring, **6** (1.15 g, 2.68 mmol) in 10 mL of dry THF was added dropwise. The mixture was stirred for 7 days at 75 °C and then quenched by addition of a few drops of water (caution! exothermic reaction, potential fire hazard). After concentration under vacuum, the residue was twice partitioned between dichloromethane and water. The combined organic phases were dried over anhydrous MgSO<sub>4</sub>, filtered, evaporated and purified by column chromatography (silica, dichloromethane) to yield 327 mg (28%) of a yellowish solid with mp 134-136 °C. HRMS (FAB, m/z): calcd for C<sub>50</sub>H<sub>44</sub>I<sub>2</sub>O<sub>4</sub> 962.1329, found 962.1498. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 1.82 (m, 4 H), 1.96 (m, 4 H), 3.36 (t, 4 H, J= 8 Hz), 3.62 (t, 4 H, J= 6 Hz), 3.76 (t, 4 H, J= 5 Hz), 4.04 (t, 4 H, J= 5 Hz), 7.19 (s, 2 H), 7.87-8.29 (m, 18 H). <sup>13</sup>C-NMR (400 MHz, CDCl<sub>3</sub>): 28.39, 29.81, 33.30, 69.19, 70.31, 71.59, 86.48, 123.51, 124.65, 124.78, 125.08, 125.75, 126.52, 127.16, 127.30, 127.53, 128.65, 129.76, 130.93, 131.44, 137.10, 153.15.

**3,4,5-Trimethoxystyrene (9).** This compound was made by a literature procedure as a yellowish oil [Gangjee, A.; Devraj, R.; Queener, S. F. *J. Med. Chem.* **1997**, *40*, 470]. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 3.81 (s, 3 H), 3.82 (s, 6 H), 5.17 (dd, 1 H, J= 10.8 Hz, J'= 0.6), 5.62 (dd, 1 H, J= 18 Hz, J'= 0.6), 6.58 (dd, 1 H, J= 10.8 Hz, J'= 10.8 Hz), 6.59 (s, 2 H).

**E,E-2,5-Bis(2-[4-(1-pyrenyl)butoxy]ethoxy)-1,4-bis((3,4,5-trimethoxystyryl)-benzene (1).** A 50 mL round-bottom flask was fitted with a condenser, charged with **8** (103 mg, 0.107 mmol), **9** (41 mg, 0.214 mmol), tri(*o*-tolyl) phosphine (5.5 mg, 0.02 mmol) and Pd(OAc)<sub>2</sub> (1 mg, 0.004 mmol), then flushed with argon. Next 10 mL of dry DMF was added, the solution was heated to 85-90 °C, and 0.05 mL of triethylamine added. After 24 h of stirring with heat, the reaction mixture was cooled to room temperature, poured into 100 mL of water, and extracted twice with ether. The solvent was evaporated and the residue subjected to column chromatography (silica, 94:6 chloroform: acetone). The isolated product fraction was evaporated under vacuum and washed with diethyl ether to give bright yellow product (90 mg, 76%, mp 65-71 °C). HRMS(FAB, m/z): calcd for C<sub>72</sub>H<sub>70</sub>O<sub>10</sub> 1094.4969, found 1094.5305. UV-vis (chloroform,  $\lambda_{\text{max}}$ /nm [ $\epsilon$ ] ): 245[50700], 269[22600], 276[36300], 330[27900],

346[37500], 387 broad[10300].  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.83 (m, 4 H), 1.94 (m, 4 H), 3.32 (t, 4 H,  $J=8$  Hz), 3.64 (t, 4 H,  $J=6$  Hz), 3.83 (overlapping s plus t, 22 H), 4.22 (t, 4 H,  $J=5$  Hz), 6.68 (s, 4 H), 7.01 (d, 2 H,  $J=16$  Hz), 7.34 (d, 2 H,  $J=16$  Hz), 7.14 (s, 2 H), 7.77 (d, 2 H,  $J=8$  Hz), 7.90-8.24 (m, 18 H).  $^{13}\text{C-NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 28.33, 29.69, 33.16, 56.04, 60.95, 69.33, 69.53, 71.44, 103.67, 122.82, 123.35, 124.64, 124.74, 124.78, 124.98, 125.74, 126.52, 127.17, 127.48, 129.10, 130.86, 131.86, 136.62, 153.30.

**1,8-Bis(2,6-dimethoxy-4-vinylphenoxy)-octane (10).** This compound was made by a literature procedure: mp 52-54 °C (lit. mp 52-53 °C[Pasco, S.; Lahti, P. M.; Karasz, F. E. *Macromolecules* **1999**, 32, 6933]).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.34-1.46 (m, 8 H), 1.76 (m, 4 H), 3.85 (m, 12 H), 3.95 (t, 4 H,  $J=7$  Hz), 5.20 (d, 2 H,  $J=12$  Hz), 5.65 (d, 2 H,  $J=18$  Hz), 6.62 (s, 4 H), 6.63 (d, 2 H,  $J=11$  Hz).

**Polymer (5).** Compounds **8** (100 mg, 0.1 mmol) and **10** (49 mg, 0.1 mmol), tri(*o*-tolyl)phosphine (6 mg, 0.02 mmol) and  $\text{Pd}(\text{OAc})_2$  (0.9 mg, 4 micromoles) were placed in a 50 mL round-bottom flask fitted with a condenser and flushed with argon. Then, 10 mL of dry DMF and 0.1 mL of tributylamine were added, and the mixture heated to 120-125 °C. After 72 h the reaction mixture was cooled to room temperature, and then poured into 100 mL of ice water. The resulting yellow, paste-like product covering the flask wall was dissolved in dichloromethane, concentrated with a stream of air, and dried under vacuum overnight to yield 50 mg (40%) of **5**. UV-vis (THF,  $\lambda_{\text{max}}/\text{nm} [\epsilon]$ ): 242[67000], 264[35500], 276[48000], 315[22600], 328[40500], 344[51300], 375 broad[10000]. GPC (THF):  $M_n=9100$ ,  $M_w=15700$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.27-143 (m, 10 H), 1.75-1.92 (m, 14 H), 3.28 (m, 6 H), 3.62 (m, 4 H), 3.85 (m, 12 H), 3.94 (m, 6 H), 4.20 (m, 4 H), 6.62 (m, 2 H), 6.70 (m, 2 H), 7.03 (m, 2 H), 7.14 (s, 1 H), 7.30 (m, 2 H), 7.79-8.26 (m, 20 H). A small residuum of vinyl end group resonances was observed at  $\delta$  5.2-5.5 in the  $^1\text{H-NMR}$ .  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ): 22.68, 25.30, 25.84, 28.33, 29.46, 29.76, 30.10, 31.61, 33.18, 34.68, 56.11, 69.32, 71.44, 73.59, 103.39, 103.83, 123.38, 124.79, 125.00, 125.76, 126.54, 127.19, 127.51, 128.58, 129.74, 130.88, 131.40, 133.03, 133.34, 136.85, 137.30, 151.09, 153.56.

**E,E-2,5-Bis(2-hydroxyethoxy)-1,4-bis(3,4,5-trimethoxystyryl)benzene (11).** This compound was made from **7** and **9** by a previously published procedure[Sierra, C. A.; Lahti, P. M. *Chem. Mater.* **2004**, 16, 55]: mp 245-247 °C.  $^1\text{H-NMR}$  ( $\text{DMSO}-d_6$ ):  $\delta$  3.67 (s, 6 H), 3.82 (overlapping s plus t, 16 H), 4.08 (t, 4 H,  $J=4$  Hz), 6.89 (s, 4 H), 7.3 (d, 2 H,  $J=16.8$  Hz), 7.45 (d, 2 H,  $J=16.8$  Hz), 7.34 (s, 2 H).

**4-(1-Pyrenyl)butyryl chloride (12).** This compound was made by literature procedures as a pale yellow solid with mp 81-83 °C (lit mp 73.5-74.5 °C[Tran, C. D.; Fendler, J. H. *J. Am. Chem. Soc.* **1980**, 102, 2923], lit mp 89-90 °C[Winnik, M. A.; Redpath, T.; Richards, D. H. *Macromolecules* **1980**, 13, 328]).  $^1\text{H-NMR}$  ( $\text{DMSO}-d_6$ ):  $\delta$  2.01 (m, 2 H), 2.46 (t, 2 H,  $J=7$  Hz), 3.32 (t, 2 H,  $J=8$  Hz), 7.90 (d, 2 H). IR (NaCl plate,  $\text{cm}^{-1}$ ): 3040, 2949, 2875, 1732, 1587, 1435, 1372, 1145, 1036, 843, 758, 720, 681; no OH stretch was observed in 3500-2500  $\text{cm}^{-1}$  region.

**E,E-2,5-Bis(2-[4-(1-pyrenyl)butyryloxy]ethoxy)-1,4-bis[2-(3,4,5-trimethoxystyryl)-benzene (2).** In a round bottom flask at 0 °C under argon were placed **11** (122 mg, 0.21 mmol) and triethylamine (0.2 mL, 1.05 mmol). After stirring for 30 min, **12** (135 mg, 0.44 mmol) was added. The reaction mixture was warmed to room temperature and allowed to stir for 24 h. Addition of hexanes to the resulting mixture precipitated a fibrous yellow solid. Filtration and precipitation from chloroform:hexanes yielded 165 mg (70%) of greenish-yellow powder with mp 162-164 °C. HRMS(FAB, m/z): calcd for  $C_{72}\text{H}_{66}\text{O}_{12}$  1122.4554, found 1122.4496.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  2.15 (m, 4 H), 2.46 (t, 4 H,  $J=7$  Hz), 3.28 (t, 4 H,  $J=7$  Hz), 3.84 (s, 4 H), 3.86 (s, 14 H), 4.22 (t, 4 H,  $J=5$  Hz), 4.55 (t, 4 H,  $J=5$  Hz), 6.72 (s, 4 H), 6.95 (d, 2 H,  $J=16$  Hz), 7.04 (s, 2 H), 7.33 (d, 2 H,  $J=16$  Hz), 7.72 (d, 2 H,  $J=8$  Hz), 7.92 (m, 10 H), 8.12 (m, 6 H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ): 26.92, 32.84, 34.20, 56.43, 61.27, 67.95, 104.02, 121.95, 122.59, 123.45, 125.05, 125.18, 125.28, 126.10, 126.97, 127.23, 127.47, 127.61, 127.74, 128.95, 129.69, 130.20, 131.13, 131.66, 133.70, 135.72, 138.30, 151.09, 153.68, 173.64. FTIR (KBr pellet,  $\text{cm}^{-1}$ ): 3035, 2934, 1735, 1580, 1507, 1419, 1322, 1244, 1127, 1005, 962, 844. UV-vis (THF,  $\lambda_{\text{max}}/\text{nm} [\epsilon]$ ): 243[94600], 264[47200], 276[70100], 327[75000], 343[97000], 397[48200].

**2,5-Diiodo-1,4-bis[2-(2-hydroxyethoxy)ethoxy]benzene (14).** This compound was made by a literature procedure as a pale yellow solid with mp 104-106 °C (lit mp 104-105.5 °C[Zhou, Q.; Swager,

T. J. Am. Chem. Soc. **1995**, *117*, 12593].  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  2.15 (br s, 2 H), 3.70 (t, 4 H,  $J=4.8$  Hz), 3.76 (s, 4 H), 3.88 (t, 4 H,  $J=4.5$  Hz), 4.12 (t, 4 H,  $J=4.7$  Hz), 7.23 (s, 2 H).

**E,E-2,5-Bis(2-(2-hydroxyethoxy)ethoxy)-1,4-bis(3,4,5-trimethoxystyryl)benzene (15).**

Compounds **9** (0.64 g, 3.3 mmol) and **14** (0.71 g, 1.32 mmol), tri(*o*-tolyl)phosphine (200 mg, 0.66 mmol) and  $\text{Pd}(\text{OAc})_2$  (30 mg, 0.13 mmol) were placed in a 50 mL round-bottom flask fitted with a condenser were flushed with argon, and 20 mL of dry DMF was added. The reaction was heated to 120 °C, and 1.2 mL of triethylamine added. After 2 days of heating, the reaction was cooled to room temperature and poured into 200 mL of water to give a dark brown precipitate that was dissolved in dichloromethane, filtered through Celite, concentrated and precipitated from dichloromethane:hexanes to yield 680 mg (77%) of yellow powder product with mp 225–228 °C. HRMS(ESI, m/z): calcd for  $\text{C}_{36}\text{H}_{46}\text{O}_{12}$  ( $M^++\text{H}$ ) 670.2996, found 670.2989.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  3.70 (t, 4 H,  $J=4.4$  Hz), 3.76 (m, 4 H), 3.87 (s, 6 H), 3.92 (overlapping s plus t, 14 H), 4.25 (t, 4 H,  $J=4.6$  Hz), 6.77 (s, 4 H), 7.06 (d, 2 H,  $J=16$  Hz), 7.34 (d, 2 H,  $J=16$  Hz), 7.15 (s, 2 H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ): 56.71, 61.00, 61.76, 69.24, 69.90, 72.57, 103.80, 111.40, 122.87, 127.70, 129.41, 133.40, 138.02, 151.02, 153.42.

**E,E-2,5-Bis(2-[2-(4-[1-pyrenyl]butyryloxy)-ethoxy]-1,4-bis(3,4,5-trimethoxystyryl)benzene (3).**

A round bottom flask containing 4-(1-pyrene)butyric acid (150 mg, 0.52 mmol) in 20 mL of fresh dry dichloromethane and 0.25 mL of dry DMF under argon was cooled to 0 °C. Then thionyl chloride (0.2 mL, 2.7 mmol) was added and the reaction was stirred for 1 h at room temperature to give a clear solution, which was then heated to reflux. After 12 h the reaction was complete according to TLC analysis. Excess thionyl chloride and solvent were then removed by distillation under reduced pressure, and the resulting solid product dissolved in a minimal amount of dichloromethane to make a solution of **12**.

In a round bottom flask under argon **15** (70 mg, 0.1 mmol) was added to 15 mL of dry dichloromethane. The suspension was stirred and cooled to 0 °C in an ice bath. Triethylamine (30 microL, 0.2 mmol) and 4-(dimethylamino)pyridine (DMAP, 64 mg, 0.52 mmol) were added. After 30 min the solution of **12** in dichloromethane was added and the reaction was allowed to stir at room temperature for 24 h. The reaction was then poured into 100 mL of water, and the organic layer separated, dried over  $\text{MgSO}_4$ , filtered and purified by column chromatography over silica gel (dichloromethane:methanol 95:5) to give 50 mg (40%) of product with mp 107–110 °C. HRMS(FAB, m/z) calcd for  $\text{C}_{76}\text{H}_{74}\text{O}_{14}$  1210.5247, found 1210.5079.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  2.15 (m, 4 H), 2.45 (t, 4 H,  $J=8$  Hz), 3.33 (t, 4 H,  $J=8$  Hz), 3.81 (t, 4 H,  $J=4$  Hz), 3.89 (overlapping s plus t, 20 H), 4.17 (t, 4 H,  $J=8$  Hz), 4.31 (t, 4 H,  $J=4$  Hz), 6.73 (s, 4 H), 6.99 (d, 2 H,  $J=16$  Hz), 7.29 (d, 2 H,  $J=16$  Hz), 7.06 (s, 2 H), 7.80 (d, 2 H,  $J=8$  Hz), 7.97 (m, 10 H), 8.12 (m, 8 H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ): 26.70, 30.95, 32.20, 33.75, 56.12, 61.27, 63.35, 69.05, 69.45, 69.95, 103.69, 122.59, 123.35, 124.75, 124.87, 124.98, 125.10, 125.97, 126.63, 127.07, 127.34, 127.46, 128.68, 129.69, 129.90, 130.13, 131.36, 133.50, 135.72, 137.30, 150.92, 153.38, 173.41. UV-vis (THF,  $\lambda_{\text{max}}/\text{nm}$  [ $\epsilon$ ]): 243[103800], 266[41300], 277[64500], 328[61000], 344[84550], 375[32300].

**1,4-Diiodo-2,5-bis(methoxymethoxy)benzene (16).** A round bottom flask containing **13** (514 mg, 1.42 mmol) in 20 mL of dry dichloromethane was cooled to 0 °C. Then, 1 mL of *N,N*-diisopropylethylamine (5.7 mmol) was added dropwise. The reaction was allowed to stir for 30 min, and then chloromethyl methyl ether (0.32 mL, 4.26 mmol) was added, turning the reaction mixture from a suspension to a clear solution after a few minutes. After 4 h of stirring at room temperature, 20 mL of water was added. The organic layer was separated, washed three times with water, dried over  $\text{MgSO}_4$ , and vacuum concentrated. Several precipitations from dichloromethane:hexanes gave 600 mg (94%) of product as light brown needles with mp 128–130 °C. MS(ESI, m/z): calcd for  $\text{C}_{10}\text{H}_{12}\text{O}_4\text{I}_2$  ( $M^++\text{H}$ ) 449.8824, found 449.8436.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  3.51 (s, 6 H), 5.15 (s, 4 H), 7.45 (s, 2 H).

**E,E-2,5-Bis(methoxymethoxy)-1,4-bis(3,4,5-trimethoxystyryl)benzene (17).** A 50 mL round-bottom flask was fitted with a condenser, charged with **16** (580 mg, 1.3 mmol), **9** (500 mg, 2.6 mmol), tri(*o*-tolyl)phosphine (79 mg, 0.26 mmol) and  $\text{Pd}(\text{OAc})_2$  (12 mg, 0.05 mmol), then flushed with argon. Then 10 mL of dry DMF and 1 mL of triethylamine were added and the reaction mixture was warmed to 105 °C, stirred for 48 h, and then cooled to room temperature. The reaction was poured into 100 mL of

water to give a yellow cloudy suspension that was extracted with dichloromethane. The organic layer was dried over MgSO<sub>4</sub>, vacuum concentrated and purified by column chromatography (silica, dichloromethane) to yield 688 mg (91%) of a reddish powder with mp 214-216 °C. This material was used without further purification for the next synthetic step. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 3.57 (s, 6 H), 3.87 (s, 7 H), 3.93 (overlapping s, 13 H), 5.27 (s, 4 H), 6.76 (s, 4 H), 7.04 (d, 4 H, J= 16 Hz), 7.33 (d, 4 H, J= 16 Hz), 7.37 (s, 2 H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 56.35, 56.44, 61.00, 95.75, 103.14, 112.83, 122.43, 127.60, 129.70, 133.42, 138.00, 150.09, 153.39.

**E,E-1,4-Bis(3,4,5-trimethoxystyryl)-2,5-dihydroxybenzene (18).** To a suspension of **17** (688 mg, 1.2 mmol) in 10 mL of ethanol was added *p*-toluenesulfonic acid monohydrate (1 g, 5.5 mmol). The reaction was stirred for 1 h at room temperature, and then 8 mL of dichloromethane was added to give a clear solution. After 24 h the reaction was treated with 50 mL of 5% aq HCl and extracted with dichloromethane, dried over MgSO<sub>4</sub>, filtered and purified by column chromatography over silica gel (dichloromethane /methanol 95:5) to give 500 mg (84%) of a light brown powder with mp 220-224 °C. MS(ESI, m/z): calcd for C<sub>28</sub>H<sub>30</sub>O<sub>8</sub> (M<sup>+</sup>+H) 494.19, found 494.20. <sup>1</sup>H-NMR (acetone-*d*<sub>6</sub>): δ 3.75 (s, 6 H), 3.89 (s, 12 H), 6.88 (s, 4 H), 7.11 (d, 2 H, J= 16 Hz), 7.44 (d, 2 H, J= 16 Hz), 7.14 (s, 2 H). <sup>13</sup>C-NMR (acetone-*d*<sub>6</sub>): 61.00, 65.14, 109.83, 128.83, 129.90, 133.70, 139.42, 143.50, 153.09, 159.39.

**E,E-2,5-Bis(4-(1-pyrenyl)butyryloxy)-1,4-bis(3,4,5-trimethoxystyryl)benzene (4).** A mixture of **17** (153 mg, 0.31 mmol), pyrenebutyric acid (200 mg, 0.69 mmol), triphenylphosphine (182 mg, 0.69 mmol), triethylamine (0.4 mL, 2.87 mmol) and 4 mL of carbon tetrachloride in 15 mL of acetonitrile was stirred at room temperature for 48 h. The solvent was evaporated to leave a black solid residue. The solid was dissolved in 20 mL of chloroform, washed with 3×40 mL of aq Na<sub>2</sub>CO<sub>3</sub>, dried over anhydrous MgSO<sub>4</sub> and evaporated under reduced pressure to give a yellow precipitate that was purified by column chromatography (silica, 95:5 dichloromethane:methanol) to yield 180 mg (56%) of a light yellow powder with mp 224-226 °C. HRMS(FAB, m/z): calcd for C<sub>68</sub>H<sub>58</sub>O<sub>10</sub> 1034.3668, found 1034.4030. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 2.40 (m, 4 H), 2.82 (t, 4 H, J= 7.2 Hz), 3.53 (t, 4 H, J= 8 Hz), 3.67 (s, 12 H), 3.78 (s, 7 H), 6.61 (s, 4 H), 6.95 (d, 2 H, J= 16 Hz), 7.01 (d, 2 H, J= 16 Hz), 7.42 (s, 2 H), 7.92-8.12 (m, 20 H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 26.98, 32.84, 33.97, 55.93, 60.95, 103.88, 120.21, 120.45, 123.18, 124.90, 125.10, 125.97, 126.93, 127.35, 127.44, 127.68, 128.75, 130.14, 130.83, 131.43, 131.87, 132.70, 135.02, 138.40, 145.89, 153.38, 171.54. UV-vis (THF, λ<sub>max</sub>/nm[ε]): 243[127000], 265[57500], 277[74400], 328[62000], 344[82000], 393[42800].

**E,E-2,5-Bis(undecanoloxy)-1,4-bis(3,4,5-trimethoxystyryl)benzene (19).** In a round bottom flask a mixture of **18** (30 mg, 0.06 mmol), undecanoic acid (34 mg, 0.18 mmol), triphenylphosphine (48 mg, 0.18 mmol), triethylamine (0.03 mL, 0.18 mmol) and 1 mL of carbon tetrachloride in 15 mL of acetonitrile was stirred at room temperature for 24 h. The solvent was evaporated to leave a black solid, which was dissolved in 20 mL of chloroform, washed with 3×40 mL of aq Na<sub>2</sub>CO<sub>3</sub>, dried over anhydrous MgSO<sub>4</sub> and evaporated under reduced pressure to give 40 mg (80%) of solid with mp 103-105 °C. HRMS (FAB, m/z): calcd for C<sub>50</sub>H<sub>70</sub>O<sub>10</sub> 830.4827, found 830.4969. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 0.87 (t, 6 H, J= 6 Hz), 1.25 (m, 24 H), 1.43 (m, 4 H), 1.83 (m, 4 H), 2.64 (t, 4 H, J= 7.6 Hz), 3.87 (s, 8 H), 3.89 (s, 16 H), 6.69 (s, 4 H), 6.94 (d, 2 H, J= 16 Hz), 7.00 (d, 2 H, J= 16 Hz), 7.37 (s, 2 H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 14.12, 22.68, 25.15, 29.30, 29.90, 31.88, 34.47, 56.11, 61.00, 64.80, 103.87, 120.14, 124.56, 127.35, 132.72, 138.43, 145.82, 153.41, 172.04. UV-vis (THF, λ<sub>max</sub>/nm[ε]): 356[24900].