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Synthesis of Oligo(1,8-pyrenylene)s: A Series of Functional Molecular Liquids

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Dedicated to the memory of Rajendra Rathore

Abstract: A monomer-through-pentamer series of oligo(1,8pyrenylene)s was synthesized using a two-step iterative synthetic strategy. The trimer, tetramer and pentamer are mixtures of atropisomers that interconvert slowly at room temperature (VTNMR analysis). They are liquids well below room temperature, as indicated by POM, DSC and SWAXS analysis. The oligomers are highly fluorescent both in the liquid state and in dilute solution and an investigation of their photohysical properties demonstrated that delocalization plays a larger role in their excited states than it does in related pyrene-based oligomers.

Introduction

Pyrene is an increasingly useful building block for the synthesis of designed pi systems, due mainly to its intense fluorescence and the sensitivity of its fluorescence to its microenvironment. Although pyrene has featured prominently in a large number of designed pi systems,^[1] only a few oligoarylenes composed *exclusively* of pyrene units have been reported. This includes, but is not limited to, dendrimers **1** and **2**,^[2] cyclic oligo(1,3-pyrenylene) **3**,^[3] poly(2,7-pyrenylene) **4**^[4] and oligo(1,6-pyrenylene)s **5** (Figure 1).^[5] Some poly(pyrene)s with varying degrees of polydispersity and integrity of the substitution pattern, as well as oligomers with mixed substitution patterns have also been reported.^[6] Oligopyrenes **1-5** all exhibit strong fluorescence, which makes them candidates for use as luminescent materials in organic optoelectronic devices.

Unlike oligo(pyrenylene)s **1-5**, which are all solids, some recently reported pyrene-containing oligoarylenes, *e.g.* **6**, were found to be liquids at room temperature.^[7] This property is very

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unusual for an aromatic molecule of its size. Combined with their luminescence, this property renders them functional molecular liquids (FML).^[8] Organic FMLs have been described as "the third generation of liquid chemicals after the first and second generations of solvent liquids and ionic liquids, respectively"^[8b] and are a rapidly-emerging class of compounds owing to their ease of processability in device fabrication (*e.g.* using painting and printing), ease of deformation within devices, high thermal stability and their ability to act as solvents for dopants.^[8] FMLs have also been used as the basis for the formation of white-emitting luminescent inks.^[8e]





Figure 1. Oligo(pyrenylene)s 1-5, pyrene-based FMLs 6 and oligo(1,8-pyrenylene)s 7.

Nakanishi's guidelines for the design of FMLs address certain key structural features that disfavor $\pi-\pi$ interactions and thus suppress solidification.^[7] These include biaryl bonds, alkoxy substituents with branching and low symmetry in the pi skeleton. The notion that some combination of the these structural features underpins the room temperature liquid behavior and our recent interest in the synthesis of designed π systems featuring 1,8-pyrenylene units^[9] fuelled work in our group aimed at the synthesis of oligo(1,8-pyrenylene)s 7. Like 6, these purely pyrene-based oligoarylenes have biaryl bonds and are adorned with alkoxy substituents. Furthermore, the high barrier to rotation about the 1,1'-bipyrenyl bond (25.8 kcal/mol)^[10] means that atropisomerism comes into play and mixtures of diastereomers will be expected starting with the trimer (7, n=1). These (or any) diastereomers will have different shapes, which would be expected to disfavor long-range ordering and thus inhibit solidification. In fact. Nakanishi's FMLs are also mixtures of diastereomers due to the presence of a stereorandom stereogenic centre in each of the eight Guerbet-alcohol-derived side chains. For example, there are eight side chains in 6b, which gives rise to 44 diastereomers (see Supporting Information). Thus, diastereoisomerism is a separate issue from branching alone, which may or may not bring with it stereochemical consequences. Finally, with multiple pyrene units in the oligo(1,8-pyrenylene)s 7, strong fluorescence would be expected, so they appear to be promising candidates for new FMLs. We report here the synthesis and characterization of the monomer through the pentamer.

Results and Discussion

Akin to Rathore's synthesis of the oligo(1,6-pyrenylene)s **5**,^[5] an iterative strategy was envisioned for the synthesis of the oligo(1,8-pyrenylene)s **7** (Scheme 1). Each iteration consists of a regioselective bromination (at the starred positions) followed by a Suzuki-Miyaura cross-coupling with an appropriate boronic ester **9**. Application of this strategy to the monomer **8**^[11] would successively give rise to the odd-numbered oligomers (**11**, **13**, **15**, *etc.*) and dimer **10** would serve as a starting point for the synthesis of the even-numbered oligomers (**12**, **14**, **16**, *etc.*). The success of this strategy hinges on the maintenance of the complete regioselectivity of the bromination step for the starred positions of each oligomer and the development of a way to gain access reliably to synthetically usefully quantities of a boronic acid/ester **9**, which comes into play during every iteration.

Synthetic work aimed at realizing the iterative strategy commenced with 4,5-dialkoxypyrenes **8a** and **8b**, which were synthesized from pyrene by *K*-region oxidation^[12] and reductive alkylation as previously described (Scheme 2).^[11] Reaction with Br₂ afforded the corresponding dibromides **17a** and **17b** in high yield. The Suzuki-Miyaura step was first tested using commercial pyrene-1-boronic acid (**18**) and this afforded 1,8-dipyren-1-ylpyrenes **19a** and **19b**. The yields were modest, but the observation that **19b** is a high-melting solid (mp >233 °C, dec) and **19a** is a room-temperature liquid was striking. For these compounds, side chain length is clearly an important

contributor to the suppression of solidification. It was therefore decided to employ decoxy groups for the synthesis of the targeted oligo(1,8-pyrenylene)s.



Scheme 1. Iterative strategy for the synthesis of oligo(1,8-pyrenylene)s.



Scheme 2. Synthesis of 1,8-dipyren-1-ylpyrenes 19a and 19b and a depiction of the two diastereomers of 19b.

The branched (chiral) alkyl groups employed by Nakanishi, which rendered his FMLs mixtures of diastereomers, were not considered here because the atropisomerism of the 1,1'bipyrenyl system was expected to result in the formation of mixtures of diastereomers. Indeed, the ¹H NMR spectra of 19a and 19b (Figure 2) exhibit two sets of signals, which is consistent with the presence of two slowly interconverting atropisomeric diastereomers, i.e. meso-19a and (±)-19a. For both compounds, the highest-field aromatic signals are a pair of singlets (no COSY cross-peaks, see Supporting Information) attributable to the K-region protons of the central pyrene unit (δ 7.53 and 7.49 ppm for **19a**; δ 7.50 and 7.47 ppm for **19b**). In both cases, the higher-field signal is slightly more intense and integration points to a 53:47 ratio of the two diastereomers. Some broadening was observed upon heating to 110 °C (Figure S1), but the system was clearly not close to coalescence. This

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is in line with the calculated barrier of 25.8 kcal/mol.^[10] For **19b**, where $\Delta v = 14.7$ Hz for the two *K*-region singlets, this barrier would correspond to a coalescence temperature (T_c) of 217 °C.

Progress with the iterative strategy could not be made with **19a** and **19b** because each of the terminal pyrene units has three sites available for electrophilic aromatic substitution. Accordingly, attention was turned to the synthesis of a boronic acid or ester of the general structure **9**. The main challenge in accomplishing this was the selective monofunctionalization of 4,5-didecoxypyrene (**8a**).



Figure 2. Aromatic region of the 300 MHz ¹H NMR spectrum of **19b** in $CDCI_3$ highlighting the clearly identifiable pairs of signals due to the *meso* and (±) diastereomers.

Monobromination of 8b with Br2 at -78 °C has been reported,^[13] but the compound was used without purification and no indication of the distribution between unbrominated, monobrominated and dibrominated products was given. Nevertheless, this result suggested that selective monobromination of 8a was achievable. Preliminary attempts to monobrominate 8a using Br₂, CuBr₂ and NBS all gave mixtures of unbrominated, monobrominated and dibrominated products under a variety of conditions. To better understand the progress of the reaction, an experiment was performed in which Br₂ was added to a CH₂Cl₂ solution of 8a (500 mg) in 0.1 equivalent portions at room temperature. TLC analysis following each addition showed that the expected new spot for monobromide 20 (R_f=0.10, 20% CH₂Cl₂/hexanes) appeared after the first addition, a little ahead of the one for 8a (R = 0.15). A second. new faster-moving spot corresponding to dibromide 17a $(R_{\rm f}=0.20)$ appeared after the addition of just 0.3 equivalents of Br₂. The starting material 8a was fully consumed only after the addition of 1.3 equivalents of Br₂ and the last vestiges of monobromide 20 disappeared after the addition of 2.2 equivalents. The addition of 10 equivalents of Br₂ or the use of neat Br₂ as the solvent does not result in further bromination.

In an attempt to delay the onset of dibromination, the reaction was performed at lower temperatures. At 0 °C and – 20 °C, dibromide **17a** again appeared after the addition of just 0.3 equivalents of Br₂. At –40 °C and –78 °C, **8a** precipitated from the reaction. Based on these results, it was decided to move forward with the addition of 1.3 equivalents of Br₂ at room

temperature, which would require the separation of just two compounds and not three. For practical purposes, slow addition of a solution of 1.3 equivalents Br_2 in CH_2Cl_2 was also found to result in the complete consumption of **8a** and the reaction could be scaled up to 5 g of **8a**. At this scale, a 73% yield of **20** was obtained along with 19% of **17a** (Scheme 3). It is worth noting that the chromatographic separation of **20** from **17a** was found to be easier than the separation of **20** from **8a**, even though the differences in R_f values did not suggest this.



Scheme 3. Synthesis of boronic ester 22, trimer 11a and pentamer 13a.

With access to multigram quantities of 20, its conversion to boronic ester 22 was investigated. Lithiation-borylation protocols were found to be unsatisfactory and, after screening various sets of conditions, it was found that Miyaura borylation using HBpin, Pd(dppf)Cl₂ and KOAc in 1,4-dioxane enabled the synthesis of 22 in 91% yield on a 1.5 g scale. The synthesis of the odd-numbered oligomers then commenced with the Suzuki-Miyaura cross-coupling between dibromide 17a and boronic ester 22, which afforded trimer 11a (77%) (Scheme 3). The use of Ba(OH)₂ instead of K₂CO₃ was found to give much better yields. No dimeric species arising from incomplete Suzuki-Miyaura reaction or protodebromination were observed (TLC, NMR analysis). As in the case of **19a** and **19b**, the ¹H NMR spectrum of 11a showed the presence of two diastereomers (see Supporting Information). Singlets for the central K-region protons were observed at δ 7.50 and 7.48 ppm, but this time the lower-field signal was slightly more intense (51:49). Again, broadening of the signals was observed at 110 °C, (Figure S1), but nothing approaching coalescence.

No TLC conditions could be found that resulted in even the slightest separation of the two diastereomers of **11a**, so the determination of which isomer is dominant presented a stiff challenge. Structures of the *meso* and (±) diastereomers (using MeO substituents instead of DecO for computational ease) were calculated at the B3LYP/6-31G(d) level of theory using a chloroform solvent model (Figure S4-5). The *meso* isomer (μ_{calc} =0.57 D) was calculated to be 0.12 kcal/mol lower in energy than the (±) isomer (μ_{calc} =0.22 D), which corresponds to a 55:45 ratio.

The bromination of 11a was not as straightforward as that of 8a. As with 8a, TLC monitoring of the addition of successive 0.1 equivalent portions of Br₂ revealed the appearance of first one faster-moving spot and then another corresponding to the formation of a monobromide and then dibromide 23. The differences in the $R_{\rm f}$ values, however, were smaller than before, which did not bode well for chromatographic separation, and the starting material spot persisted until the addition of 1.9 equivalents of Br₂ (cf. 1.2 equivalents for 8a). Additionally, while 8a was found to be resistant to over-bromination, exceeding 2 equivalents of Br₂ almost immediately resulted in overbromination of 11a, as indicated by TLC (appearance of a new spot ahead of dibromide 23). The best result was obtained when **11a** was reacted with 2.03 equivalents of Br₂. This afforded dibromide 23 in 78% yield after repeated chromatography. Suzuki-Miyaura reaction of 23 with boronic ester 22 then afforded pentamer 13a (84%), which has six possible diastereomers (statistical ratio = 1:2:2:1:1:1, see Supporting Information) arising from the four axes of asymmetry.

For the even-numbered oligomers, dimer **10a** was required. This compound was synthesized using three methods (Scheme 4). First, Suzuki-Miyaura coupling of bromide **20** with boronic ester **22** gave **10a** in 64% yield. Second, Feringa's PEPPSI-iPrcatalyzed homocoupling^[14] of bromide **20** delivered **10a** in 94% yield. Finally, intermolecular Scholl reaction of monomer **8a** using Rathore's DDQ/MeSO₃H method^[15] proceeded in 37% yield. Although the yield of the latter reaction is substantially lower than those of the first two, it is attractive from a practical perspective. It uses a less precious starting material, is trivially easy to perform and is finished within seconds. Higher oligomers (up to hexamer) could also be observed by MALDI-MS and trimer **11a** could be reliably isolated from this reaction in up to 17% yield.



Scheme 4. Synthesis of dimer 10a and tetramer 12a.

Dimer **10a** underwent bromination smoothly using 2.0 equivalents of Br_2 to afford dibromide **24** in 88% yield. When a small excess (up to 3 equiv) of Br_2 was employed, overbromination was not a problem. Instead, a new bright yellow

compound with a much lower R_f value began to form. It was never formed in sufficient quantities to enable the acquisition of an NMR spectrum, but MS analysis (m/z = 902; most abundant signal for $C_{52}H_{54}Br_2O_4$) was consistent with one of the 4,5didecoxypyrene units having been converted to a pyrene-4,5dione unit. Tetramer **12a** was obtained in 71% yield upon Suzuki-Miyaura reaction of dibromide **24** with boronate **22**. This oligomer has four possible diastereomers (statistical ratio = 1:1:1:1, see Supporting Information) arising from the three axes of asymmetry.

The use of aryl iodides instead of bromides was investigated as a possible way of improving the yields of the Suzuki-Miyaura cross-coupling reactions. Monomer 8a was found to undergo rapid (20 min) and fully regioselective diiodination upon reaction with I2, Hg(OAc)2 to afford diiodide 21 (88%). Upon increasing the reaction time to 2 h, the yield plummeted to 50%. The drop in yield is clearly due to a dealkylation/oxidation reaction as pyrene-4,5-dione was isolated. In fact, this diketone is also present at the end of the 20-minute reaction (TLC analysis). The use of the diiodide 21 in the Suzuki-Miyaura reaction with boronic ester 22 led to a significant improvement of the yield trimer 11a (91%) (Scheme 3). The same improvement could not be achieved for higher oligomers because attempted iodination of dimer 10a and trimer 11a resulted in rapid and complete consumption of the starting materials to give mainly TLC immobile compounds. Clearly, the ease of the dealkylation/oxidation process increases with the size of the oligomer.

A key concern with tetramer 12a and pentamer 13a was the ability to assess purity. The presence of four and six diastereomers, respectively (see Supporting Information), complicates the NMR spectra to the point that it is impossible to tell whether they are contaminated with lower oligomers (with or without bromine atoms), which might arise from incomplete Suzuki-Miyaura reaction and/or protodebromination. Using a number of standard TLC solvent systems, e.g. 10:90 dichloromethane / hexanes, dimer 10a through pentamer 13a were barely distinguishable (Figure 3A, left). After extensive experimentation, it was found that the use of 5:5:90 toluene / dichloromethane / hexanes gave far better separation (Figure 3A, right). This allowed for more effective chromatography and, coupled with the intense fluorescence of the oligomers (see below), enabled visual assessment of purity. To demonstrate this point, a 1:100 mixture of 11a:12a was prepared and the minor component was clearly visible to the naked eye (Figure 3B).

MS analysis using various techniques was initially very problematic due to extensive fragmentation, but it was ultimately discovered that LC-MS with APPI(+) ionization gave very reliable spectra, but only when the standard solvent system (90% acetonitrile / toluene) was changed to 90% isopropanol / toluene and the injection temperature was maximized. Under these conditions, no signals attributable to dealkylated compounds or lower oligomers arising from biaryl cleavage were observed.

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Figure 3. A) Thin-layer chromatograms of monomer 8a (M), dimer 10a (D), trimer 11a (T), tetramer 12a (Te), pentamer 13a (P) and a co-spot (C) of the five oligomers developed with 365 nm light, run with 10:90 CH₂Cl₂/hexanes (left) and with 5:5:90 toluene/CH₂Cl₂/hexanes (right). B) Thin-layer chromatogram of trimer 11a at *ca.* 0.1 (A), 0.01 (B) and 0.001 (C) mg/mL, followed by tetramer 12a at *ca.* 0.1 mg/mL (D) and then a 1:100 mixture of 11a:12a (E).

It is interesting to note that Rathore's monomer through pentamer series of oligo(1,6-pyrenylene)s 5,^[5] which may also appear to be candidates for FMLs, are all solids with melting points that increase steadily from monomer (92-93 °C) to pentamer (198-200 °C). The oligo(1,8-pyrenylene)s 8a, 10a-13a behave very differently. The monomer 8a is a low-melting solid (mp=38.4-39.5 °C) and the dimer remains a supercooled liquid for as long as six months after purification before eventually crystallizing (mp=30-34 °C). The trimer 11a, tetramer 12a and pentamer 13a are all liquids that have never solidified. One sample of trimer 11a has remained a liquid after ambient aging for over 7 years. No crystallization peaks were observed in DSC traces for 11a-13a even after annealing at -42 °C for 12 hours (Figure 4),^[8c] which further supports the notion that these compounds are in fact room temperature liquids and not supercooled liquids.



Figure 4. DSC thermograms for trimer 11a (top pair), tetramer 12a (middle pair) and pentamer 13a (bottom pair) without annealing (black lines) and after annealing at -42 °C for 12 h (red lines). Scale bar = 0.2 W/g for 11a, 0.2 W/g for 12a and 0.3 W/g for 13a.

The total absence of birefringence in samples of **11a-13a**, as observed by polarized optical microscopy (POM) (Figure 5), provided further evidence that these compounds are isotropic liquids at room temperature.



Figure 5. Optical microscopy (top) and polarized optical microscopy (bottom) for 11a (left), 12a (middle) and 13a (right).

Small- and wide-angle X-ray scattering (SWAXS) measurements of trimer **11a** showed no features at all in the small-angle range and just very broad peaks at 21.0° and 42.5° in the wide-angle region (Figure 6). The former corresponds to a distance of 4.23 Å, which is typical of an alkyl halo,^[8d] and the peak at 42.5° is likely the corresponding second order peak (corresponds to a distance of 4.25 Å). The absence of any sharp peaks is indicative of the absence of long-range molecular ordering, which speaks to **11a** being a liquid. SWAXS was not measured for **12a** and **13a** due to insufficient sample sizes, but the consistency of their DSC and POM suggest that they are also liquids.



Figure 6. Small- (inset) and wide-angle X-ray scattering of trimer 11a.

An aspect of Nakanishi's FMLs, *e.g.* **6**, that does not appear to have been addressed is that they are mixtures of diastereomers by virtue of the presence of a stereorandom stereogenic centre in each of the side chains. Oligo(1,8pyreneylene)s **11a–13a** are also mixtures of diastereomers, but this arises due to axial chirality (atropisomerism in the pi skeleton. Atropisomerism in the oligo(1,6-pyrenylene)s **5** was also not addressed, but based on the appearance of their NMR spectra, the trimer, tetramer and pentamer are clearly mixtures of diastereomers. The fact that they are increasingly highmelting solids may be attributable to the presence of alkyl instead of alkoxy side chains and the more linear (1,6)substitution pattern of the pyrene units vs. the more bent (1,8)for **11a-13a**. Based on the existing evidence, it is difficult to assess the relative importance of the various factors that contribute to keeping **11a-13a** in the liquid state.

High thermal stability and low volatility of **11a** was revealed by thermogravimetric analysis (TGA), where no loss of mass was observed until *ca*. 325 °C (Figure 7). A 35% loss of mass was observed starting at 325 °C, followed by an 18% loss of mass starting at 560 °C. The first event is consistent with the loss of four of the six decyl side chains (36.7% of the initial mass) and the second loss of mass agrees very well with the cleavage of the remaining two decyl groups (18.3% of the initial mass). TGA of the tetramer **12a** and pentamer **13a** (Figures S2, S3) were similar to that of **11a**, showing the ultimate loss of *ca*. 55% of the original mass (all of the alkyl groups). For these compounds, a slight (3-6%) loss of mass was observed prior to 325 °C.



Figure 7. TGA trace for trimer 11a.

The UV-vis and emission spectra for pure liquid samples are shown in Figures 8 and 9. The neat liquid oligomers 11a-13a appear highly fluorescent to the naked eye under a UV lamp and also fluoresce visibly in ambient light. These optically opaque liquids present experimental challenges in the acquisition of spectroscopic data to characterize their ground and excited state properties. The absorption spectra (Figure 8, Table 1) were obtained using a thin film on the surface of a cuvette and the emission spectra (Figure 9, Table 2) were acquired using a front-face geometry as described in the experimental section. The determination of quantum yields in this manner can have large errors and often there are issues with the reproducibility of the quantum yield data. Thus, initial characterization of the excited states using dilute solutions in cyclohexane and conventional protocols was undertaken. As discussed below, the absorption and emission spectra closely resemble those obtained using dilute solutions in terms of band shapes and energetics. More detailed studies of the photophysics of the neat liquids **11a-13a** will be undertaken in the near future.



Figure 8. Normalized absorption spectra of trimer 11a (green), tetramer 12a (purple) and pentamer 13a (black) as neat liquid thin films in transmission mode.



Figure 9. Normalized fluorescence spectra of trimer **11a** (green), tetramer **12a** (purple) and pentamer **13a** (black) as neat liquid thin films measured using front-face emission. $\lambda_{exc} = 350$ nm.

UV-vis and emission spectra obtained from dilute solutions of **8a** and **10a-13a** in cyclohexane are shown in Figures 10 and 11, and spectroscopic data are summarized in Tables 1 and 2. The UV-vis spectrum of **8a** is dominated by three intense overlapping π - π^* transitions (Bands 1–3) and their associated vibronic progressions. The most intense transitions for the structured band envelopes are observed at at 243 nm (41152 cm⁻¹), 281 nm (35587 cm⁻¹), and 347 nm (28820 cm⁻¹) along with weak transitions at 357 nm (28011 cm⁻¹) and 376 nm (26595 cm⁻¹). The emission spectrum for **8a** (Figure 10) is complex and highly structured, comparable to the emission spectrum of pyrene. Taken together, the photophysical properties of **8a** are analogous to those found for pyrene.^[16]



Figure 10. Absorption spectra of monomer 8a (blue), dimer 10a (red), trimer 11a (green), tetramer 12a (purple) and pentamer 13a (black) in oxygen-purged cyclohexane solution.



Figure 11. Emission spectra of cyclohexane solutions of monomer 8a (blue), dimer 10a (red), trimer 11a (green), tetramer 12a (purple) and pentamer 13a (black) in oxygen-purged cyclohexane solution. λ_{exc} = 340 nm (8a, 10a, 11a) or 350 nm (12a, 13a).

The following observations are discernable from the UV-vis spectral data: (a) the vibronic resolution observed in **8a** diminishes in successive oligomers and is essentially all gone once the trimer **11a** has been reached, (b) the band maxima at 357 ± 1 nm, 288 ± 1 nm and 247 ± 1 nm for **10a-13a** are all redshifted from the analogous bands in **8a** by 834 ± 34 cm⁻¹, 865 ± 121 cm⁻¹ and 707 ± 82 cm⁻¹, respectively; (c) the spectral band envelope at 355 nm gains intensity on going from **10a** to **12a** and then levels off; (d) the energetics of the π - π transitions at 247 nm (40485 cm⁻¹), 288 nm (34722 cm⁻¹), and 357 (28010 cm⁻¹) for **10a-13a** do not change significantly (Table 1).

The absorption spectra of **11a-13a** as neat liquids closely resemble those obtained from dilute solutions, exhibiting three broad and intense bands at 365 ± 1 nm, 291 ± 1 nm and 249 ± 1 nm. These bands are only slightly red-shifted from the corresponding bands in the solution spectra, *i.e.* by 613 ± 38 cm⁻¹, 357 ± 59 cm⁻¹ and 324 ± 162 cm⁻¹, respectively. The small magnitude of these

changes indicates a very low degree of pyrene-pyrene interactions.

Table	1.	Wavelength	maxima	$\lambda_{A,max}$	for	8a	and	10a-13a	in	cyclohexane
solution and for 11a-13a as neat liquids [in square brackets].									7	

Compound	Band 1 (nm)	Band 2 (nm)	Band 3 (nm)
Monomer 8a	347	281	243
Dimer 10a	357	287	247
Trimer 11a	357 [365]	288 [291]	247 [248]
Tetramer 12a	357 [365]	288 [291]	247 [250]
Pentamer 13a	358 [366]	289 [292]	248 [250]

Table 2. Fluorescence and photophysical data for 8a and 10a-13a in deoxygenated cyclohexane solution and fluorescence data for 11a-13a as neat liquid thin films (in square brackets).

Compound	$\lambda_{F,max}$ (nm)	φ _F	$\tau_{F} \ (ns)$	$k_{R} \left(s^{-1} \right)$	$k_{NR} (s^{-1})$
Monomer 8a	379, 401, 424	0.20±0.01	39±3	5.1×10 ⁶	2.0×10 ⁷
Dimer 10a	429	0.74±0.08	2.80±0.03	2.6×10 ⁸	9.3×10 ⁷
Trimer 11a	444 [463]	0.80±0.04	2.71±0.01	3.0×10 ⁸	7.4×10 ⁷
Tetramer 12a	453 [467]	0.80±0.04	2.2±0.1	3.6×10 ⁸	9.5×10 ⁷
Pentamer 13a	457 [471]	0.80±0.01	2.2± 0.1	3.6×10 ⁸	9.5×10 ⁷

The emission spectral profiles for 10a-13a are distinctly different from the highly structured emission spectrum of 8b. The emission spectra for 10a-13a have similar emission band shapes, which shift to longer wavelength as the oligomer grows in size: **10** (λ_{em} = 429 nm (23310 cm⁻¹): **11** (λ_{em} = 444 nm (22520 cm $^{-1}$): 12 (λ_{em} = 453 nm (22075 cm $^{-1}$): and 13 (λ_{em} = 457 nm (21880 cm⁻¹). For 10a-13a, the following trends are evident from the data given in Table 2: (a) ϕ_F increases from 0.74 to 0.80 and levels off at trimer **11a**; (b) τ_F decreases from 2.8 ns to 2.2 ns and levels off at tetramer 12a; (c) the radiative rate constant (k_r) increases from 2.6 x 10⁸ s⁻¹ to 3.6 x 10⁸ s⁻¹ and levels off at tetramer 12a; and (d) the rate constant for non-radiative decay, $(k_{nr} \sim 9 \times 10^7 \text{ s}^{-1})$ is more or less constant even though the energy gap changes from 23310 cm⁻¹ for **10a** to 21880 cm⁻¹ for 13a. A quantitative analysis of the spectroscopic data to delineate the microscopic origin that underlies the photophysical properties is accommodated by the proposed mechanism described below.

In going from the monomer **8a** to the oligomers **10a-13a**, a broad absorption feature at *ca*. 360 nm emerges, which is absent in **8a**. The oligomers contain pyrene units that are linked by C–C bonds, thereby providing a structural basis for π interchromophoric coupling that mediates electron delocalization.

In the ground state, each 1,1'-bipyrenyl unit of the oligomers **10a-13a** adopts a non-coplanar orientation characterized by a dihedral angle (θ) between pyrenyl planes, which represents a compromise between steric repulsion and π -electron delocalization.^[17]

Absorption of a photon occurs on an ultrafast time scale ($\sim 10^{15}$ s) to form the Franck Condon excited state, which possesses the electronic coordinates appropriate for the excited state with the nuclear and solvent coordinates still in their ground state coordinates. The absorption energy is given by:

$$E_{abs} = \Delta G_{es} + \lambda_t + E(\theta) \qquad [1]$$

where ΔG_{es} is the free energy of the excited state and λ_t is the total reorganization energy, which includes the vibrational (λ_{vib}) and solvent reorganization (λ_o) energies. The parameter $E(\theta)$ is the energy component that depends on the dihedral angle. $E(\theta)$ contains contributions for the extent of π delocalization between the ring systems and reflects the distribution of rotational conformers that exist in the ground state.^[18]

With time, the atomic nuclei that make up the chromophore and the solvent orientations in the Franck-Condon excited states will adjust their orientations to minimize the potential energy of the thermalized excited state. The lowest lying excited states of 10a-13a decay primarily through radiative decay (Table 2). The emission energies move to longer wavelength as the number of monomer units of the oligomer increases. The kinetics are mono-exponential, which is consistent with emission coming from a very narrow conformational distribution. Taken together, it can be inferred that there is a substantial structural change on going from the Franck-Condon state to the emitting state, presumably due to a reduction of the dihedral angle. A decrease of the dihedral angle in the excited state would allow the system to more effectively delocalize the excited electron. Delocalization reduces bond length changes in the excited state and thus lowers the excited state energy on going from 10a to **13a.** If true, one would anticipate that the transition moment (M)should correlate with the number of monomer units in the oligomers. The rate constant for radiative decay is given by

$$k_r = \left(\frac{64\pi^4 n^2}{3\hbar}\right) \left|\vec{M}\right|^2 \langle \nu^{-3} \rangle^{-1} \qquad [2]$$

where $\langle v^{-3} \rangle^{-1} \cong (E_{em})^3$, and the transition moment \vec{M} is given by:

$$\overrightarrow{M} = \overrightarrow{\mu} \langle \psi^* | \psi \rangle \quad [3]$$

The transition moments were calculated for **10a** (1.31 D), **11a** (1.48 D), **12a** (1.60 D) and **13a** (1.74 D) using the experimental spectral data and Eq. 2, and they do indeed correlate with the number of monomer units in the oligomers.

The spectroscopic properties of π -conjugated oligomers are often used to predict the properties at the polymeric limit.^[19] The basis of the analysis is the linear evolution of the spectroscopic energies with $\cos[\pi/(n+1)]$ where n is the number of monomer units that make up the oligomer. Plots of the onset energies for the 360 nm absorbance $vs \cos[\pi/(n+1)]$ for **10a-13a** were found to exhibit a linear trend with a slope of $-0.60 (\pm 0.05)$, which is very close to the slope reported by Rathore for oligo(1,6-pyrenylene)s **5** (-0.56) (Figure S9).^[5] Additionally, plots of the emission energies vs $\cos[\pi/(n+1)]$ for **10a-13a** were also found to be linear with a slope of -0.50, but this is a factor of 2 larger than the corresponding slope for oligo(1,6-pyrenylene)s **5** (-0.26) (Figure S10). These observations indicate that delocalization plays a larger role in the excited states of **10a-13a** than it does in **5**. The more extensive delocalization in the excited states of **10a-13a** may ultimately prove to be important when these compounds are used as materials in organic electronic devices.

Conclusions

Oligo(1,8-pyrenylene)s 8a, 10a-13a were synthesized using a two-step iterative synthetic strategy. The trimer 11a, tetramer 12a and pentamer 13a are room temperature liquids, which are intensely fluorescent in dilute solution ($\phi_F = 0.80$) and also in the liquid state. Like other FMLs, several factors likely contribute to the suppression of solidification in 11a-13a. The 1,8 substitution pattern of pyrene units and the presence of mixtures of 2, 4 and 6 diastereomers (atropisomers), respectively, may well be among them. With regard to the issue of diastereoisomerism, it is distinct from side chain branching (an existing guideline for the design of FMLs) and a prominent feature of other FMLs. As such, it deserves to be considered in the context of future FML design. Photophysical studies of 11a-13a in dilute solution indicate that interchromphoric coupling manifests itself in radiative decay and that delocalization plays a larger role in the excited states than for Rathore's oligo(1,6-pyrenylene)s 5. Work aimed at the use of 11a-13a as solvents for chemical reactions and as functional materials is underway.

Experimental Section

Commercial reagents and solvents were used without purification. Pd(PPh₃)₄ was prepared^[20] and used before discoloration occurred (within 7 d; storage under Ar in a freezer). ¹H and ¹³C NMR spectra were recorded on a Bruker 300 MHz AVANCE III or Bruker AVANCE 500 MHz spectrometers. High-resolution APPI-TOF-MS were recorded on a GCT Premier Micromass Technologies instrument. Thermogravimetric analysis was performed on a Waters TGA-Q-500 instrument. Differential scanning calorimetry was measured using a Mettler Toledo DSC 1 STAR system. Absorption spectra were measured in cyclohexane solutions using a Cary Bio UV-vis spectrophotometer manufactured by Varian. Fluorescence spectra were measured in oxygen-free cyclohexane solution, using a Photon Technologies International (PTI) RF-M2004 fluorescence spectrometer, with excitation wavelengths of 340 nm (8a, 10a and 11a) or 350 nm (12a and 13a). Oxygen was removed from these solutions by sparging with Ar. Solutions for the fluorescence measurements were prepared to obtain an absorbance of 0.25 to 0.35 at the excitation wavelength. Fluorescence quantum yields were determined using the relative method,^[21] using 9,10-diphenylanthracene in cyclohexane as the quantum yield standard $(\phi_{\rm F} = 0.90)$.^[21] Fluorescence lifetimes were measured on the same samples used for fluorescence spectra measurements, using a Photon Technologies International instrument, which is based on the stroboscopic optical boxcar technique.^[22] Absorption spectra of the neat



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liquids of 11a-13a were measured on samples prepared by depositing highly concentrated solutions of the liquids in cyclohexane on the front surface of thin 1 mm path length quartz cuvettes layed flat, with the solvent allowed to evaporate to leave a thin, transparent film of the liquid, which allowed for the measurement of the absorption spectrum in transmission mode. Fluorescence spectra of the neat liquids of the 11a-13a were measured as thin films manually spread directly on the front surface of the thin 1 mm path length quartz cuvettes, which were placed in the fluorimeter sample holder at 45° to the both the excitation light and emission collection path, in a front-face emission configuration with 350 nm excitation. Density functional theory (DFT) calculations were performed with the Gaussian 16 software package,^[23] using the B3LYP functional in conjunction with the 6-31G(d) basis set. SWAXS data were collected on a 2 mm thick sample held horizontally using a Siemens D-5000 $\theta\text{-}\theta$ diffractometer equipped with a copper target X-ray tube and a diffracted beam monochromator. The divergence and anti-scatter slits were set to 1° and the receiving slit was set to 0.6 mm. Data was collected every 0.05° in scattering angle with a 4 s count time.

1,8-Dibromo-4,5-didecoxypyrene (17a): To a solution of 4,5didecoxypyrene $(\boldsymbol{8a})^{[11]}$ (5.00 g, 9.71 mmol) in CH_2Cl_2 (250 mL) was added bromine (3.41 g, 21.4 mmol). The reaction was stirred at room temperature for 5 min. Excess bromine was quenched by the addition of saturated sodium thiosulfate solution (150 mL). The layers were separated and the aqueous phase was extracted with CH2Cl2 (3×100 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The resulting brown solid was subjected to column chromatography (10% CH₂Cl₂/hexanes) to afford 1,8-dibromo-4,5-didecoxypyrene (17a) (6.27 g, 96%) as a pale-yellow solid. Rf (20% CH2Cl2/hexanes) = 0.90; mp = 79.3–80.5 °C (recrystalized from ethanol); ¹H NMR (CDCl₃, 300 MHz) δ = 8.52 (s, 2H), 8.36 (d, J=8.5 Hz, 2H), 8.27 (d, J=8.5 Hz, 2H), 4.31 (t, J=6.7 Hz, 4H), 2.00-1.90 (m, 4H), 1.64-1.56 (m, 4H), 1.45-1.23 (m, 24H), 0.89 (t, J=6.7 Hz, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ = 143.78, 130.72, 129.43, 128.70, 127.47, 123.48, 120.85, 119.91, 73.90, 31.92, 30.53, 29.67, 29.61, 29.55, 29.36, 26.27, 22.70, 14.13 ppm; HRMS [APPI(+)], calcd for $C_{36}H_{48}^{81}Br^{79}BrO_2$ ([M]⁺): 674.2034, found: 673.2004.

1,8-Dibromo-4,5-dimethoxypyrene (17b): To a solution of 4,5dimethoxypyrene (8b)^[11] (1.00 g, 3.81 mmol) in CH₂Cl₂ (30 mL) was added bromine (1.34 g, 8.37 mmol). The reaction was stirred at room temperature for 5 min. Excess bromine was guenched by the addition of saturated sodium bisulfite solution (25 mL). The layers were separated and the aqueous phase was extracted with CH₂Cl₂ (3×100 mL). The combined organic layers were washed with water (30 mL), washed with brine (30 mL), dried over anhydrous Na2SO4 and the solvent was removed under reduced pressure. The resulting brown solid was subjected to column chromatography (10% CH2Cl2/hexanes) to afford 1,8-dibromo-4,5-dimethoxypyrene (17b) (1.52 g, 95%) as a white solid. R_f (40% CH₂Cl₂/hexanes) = 0.60; mp = 212–214 °C; ¹H NMR (CDCl₃, 300 MHz) δ = 8.51 (s, 2H), 8.35 (d, J=8.4 Hz, 2H), 8.27 (d, J=8.4 Hz, 2H), 4.19 (s, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ = 144.45, 130.79, 129.45, 128.14, 127.46, 123.46, 120.70, 120.09, 61.18 ppm; HRMS [APPI(+)], calcd for C₁₈H₁₂⁸¹Br⁷⁹BrO₂ ([M]⁺): 419.9185, found: 419.9184.

1,8-Dipyren-1-yl-4,5-didecoxypyrene (19a): A 50 mL round-bottomed flask equipped with a side arm and capped with a rubber septum was charged with pyrene-1-boronic acid **(18)** (0.091 g, 0.037 mmol), 1,8-dibromo-4,5-didecoxypyrene **(17a)** (0.101 g, 0.150 mmol), K₂CO₃ (0.414 g 3.00 mmol), 1,4-dioxane (4 mL) and water (1 mL). The resulting slurry was subjected to four freeze-pump-thaw cycles before Pd(PPh₃)₄ (0.0036 g, 0.031 mmol) was added under a positive pressure of N₂. The flask was then resealed with a rubber septum and heated at 80 °C in an oil bath for 16 h. After cooling to room temperature, the solvent was

removed under reduced pressure and the residue was subjected to column chromatography (2% CH2Cl2/hexanes) to yield 1,8-dipyren-1-yl-4,5-didecoxypyrene (19a) (0.037 g, 27%) as a pale yellow-green viscous liquid. $R_{\rm f}$ (20% CH₂Cl₂/hexanes) = 0.60; ¹H NMR (CDCl₃, 500 MHz) δ =8.760 and 8.757 (2×d, J=8.0 Hz, 2H), 8.283 and 8.278 (2×d, J=7.8 Hz, 2H) or 8.28 (dd, J=7.8, 12.8 Hz, 2H), 8.22-8.18 (m, 2H), 8.21 (d, J=7.9 Hz, 2H), 8.14-8.08 (m, 8H), 8.00 and 7.99 (2×t, J=7.6 Hz, 2H), 7.872 and 7.866 (2×d, J=9.3 Hz, 2H), 7.73 and 7.67 (2×d, J=9.3 Hz, 2H), 7.53 and 7.49 (2×s, 2H), 4.54 (t, J=6.7 Hz, 4H), 2.17-2.10 (m, 4H), 1.78-1.72 (m, 4H), 1.56–1.50 (m, 4H), 1.48–1.25 (m, 20H), 0.95–0.85 (m, 6H); NMR (CDCl₃, 125 MHz) δ = 144.32, 136.22, 136.19, 135.78, 131.45, 130.98, 130.88, 130.07, 129.96, 129.30, 129.24, 129.05, 129.03, 128.94, 128.87, 127.57, 127.45, 126.03, 125.78, 125.21, 125.02, 124.79, 124.48, 123.31, 123.25, 119.36, 119.28, 74.12, 32.02, 30.83, 29.84, 29.76, 29.48, 26.51, 22.80, 14.22 ppm (only 27 of the 48 expected aromatic signals and only 9 of the 20 expected aliphatic signals observed); HRMS [APPI(+)], calcd for $C_{68}H_{66}O_2$ ($[M]^+$): 914.5063, found: 914.5070.

1,8-Dipyren-1-yl-4,5-dimethoxypyrene (19b): A 50 mL round-bottomed flask equipped with a side arm and capped with a rubber septum was charged with pyrene-1-boronic acid (18) (0.469 g, 1.91 mmol), 1,8dibromo-4,5-dimethoxypyrene (17b) (0.200 g, 0.476 mmol), K₂CO₃ (2.11 g 15.3 mmol), 1,4-dioxane (10 mL) and water (2 mL). The resulting slurry was subjected to three freeze-pump-thaw cycles before Pd(PPh₃)₄ (0.0176 g, 0.152 mmol) was added under a positive pressure of N₂. The flask was then resealed with a rubber septum and heated at 100 °C in an oil bath for 19 h. After cooling to room temperature, the mixture was diluted with CH_2CI_2 (100 mL). The resulting solution was washed with H₂O (3×100 mL), washed with brine (200 mL), dried over anhydrous MgSO₄ and the solvent was removed under reduced pressure. The residue was preadsorbed on silica gel and subjected to column chromatography (40% CH₂Cl₂/hexanes) to yield 1,8-dipyren-1-yl-4,5dimethoxypyrene (19b) (0.194 g, 38%) as a pale yellow solid. $R_{\rm f}$ (40%) CH₂Cl₂/hexanes) = 0.31; ¹H NMR (CDCl₃, 300 MHz) δ = 8.729 and 8.727 (2×d, J=8.0 Hz, 2H), 8.251 and 8.245 (2×d, J=7.8 Hz, 2H) or 8.25 (dd, J=7.8, 1.7 Hz, 2H), 8.20-8.13 (m, 2H), 8.19 (d, J=8.0 Hz, 2H), 8.12-8.04 (m, 8H), 7.97 and 7.96 (2×t, J=7.6 Hz, 2H), 7.84 and 7.83 (2×d, J=9.3 Hz, 2H), 7.69 and 7.63 (2×d, J=9.2 Hz, 2H), 7.50 and 7.47 (2×s, 2H), 4.38 (s, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ = 144.95, 136.07, 136.04, 135.98, 135.91, 131.42, 130.92, 130.86, 130.01, 129.95, 129.94, 129.29, 129.23, 128.86, 128.80, 128.43, 128.41, 127.54, 127.41, 127.40, 126.01, 125.96, 125.92, 125.68, 125.19, 125.00, 124.78, 124.73, 124.43, 124.35, 123.24, 123.18, 119.13, 119.06, 61.38 ppm (only 34 of the 48 expected aromatic signals observed); HRMS [APPI(+)], calcd for $C_{50}H_{30}O_2$ ([M]⁺): 662.2246, found: 662.2299.

1-Bromo-4,5-didecoxypyrene (20): To a solution of 4,5-didecoxypyrene (8b)^[11] (5.00 g, 9.77 mmol) in CH₂Cl₂ (100 mL) in a 500 mL roundbottomed flask was added dropwise a solution of bromine (2.03 g, 12.7 mmol) in CH₂Cl₂ (127 mL, 0.1 M) over 35 min. The resulting solution was transferred to a separatory funnel, washed with water (100 mL), washed with brine (100 mL), dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The resulting pale pink-orange solid was adsorbed on silica gel and subjected to column chromatography (1% CH₂Cl₂/hexanes) to afford 1,8-dibromo-4,5didecoxypyrene (17a) (1.26 g, 19%) and 1-bromo-4,5-didecoxypyrene (20) (4.20 g, 73%) as a waxy white solid. R_f (1% CH₂Cl₂/hexanes) = 0.10; mp=45.4-46.8 °C (recrystallized from ethanol); ¹H NMR (CDCI₃, 300 MHz) δ = 8.52 (dd, J=7.8, 1.0 Hz, 1H), 8.42 (d, J=9.2 Hz, 1H), 8.33 (d, J=8.5 Hz, 1H), 8.24 (d, J=8.5 Hz, 1H), 8.17 (dd, J=7.8, 0.7 Hz, 1H), 8.15 (d, J=9.0 Hz, 1H), 8.05 (t, J=7.7 Hz, 1H), 4.34 (t, J=6.7 Hz, 4H), 2.01-1.88 (m, 4H), 1.64-1.58 (m, 4H), 1.41-1.22 (m, 24H), 0.87 (t, J=6.7 Hz, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ = 144.15, 143.76, 130.94, 130.11, 129.51, 129.11, 128.93, 128.54, 126.55, 125.88, 124.85, 124.07, 122.26,

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120.18, 120.18, 119.34, 73.88, 73.85, 31.95, 30.61, 30.59, 29.71, 29.64, 29.60, 29.59, 29.38, 26.33, 22.72, 14.15 ppm (only 13 of the 20 expected aliphatic signals observed); HRMS [APPI(+)], calcd for $C_{36}H_{49}{}^{81}BrO_2$ ([M]⁺): 592.2916, found: 592.2893.

2-(4,5-Didecyloxypyren-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (22): A 250 mL round-bottomed flask equipped with a side arm and capped with a rubber septum was charged with 1-bromo-4,5didecoxypyrene (20) (1.50 g, 2.53 mmol), 1,4-dioxane (50 mL), KOAc (0.744 g, 7.58 mmol) and HBPin (0.970 g, 7.58 mmol). The mixture was subjected to three freeze-pump-thaw cycles before Pd(dppf)₂Cl₂ (0.092 g, 0.13 mmol) was added under a positive pressure of nitrogen. The mixture was heated at 80 °C in an oil bath for 4 h. The rubber septum was then replaced with a distillation head and the majority of the solvent was removed by distillation. After cooling, the resulting brown sludge was dissolved in CH₂Cl₂ (200 mL) and the resulting solution was washed with water (100 mL), washed with brine (100 mL), dried over anhydrous magnesium sulphate. The solvent was removed reduced pressure and the crude mixture was subjected to column chromatography (20% CH₂Cl₂/hexanes) to afford 2-(4,5-didecoxypyren-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (22) as a pale brown oil (1.47 g, 91%). Rf (50% CH_2CI_2 /hexanes) = 0.60; ¹H NMR (CDCI₃, 300 MHz) δ = 9.05 (d, J=9.1 Hz, 1H), 8.55 (d, J=7.9 Hz, 1H), 8.51 (d, J=7.9 Hz, 1H), 8.46 (d, J=7.9 Hz, 1H), 8.16 (d, J=7.7 Hz, 1H), 8.11 (d, J=9.3 Hz, 1H), 8.02 (t, J=7.7 Hz, 1H), 4.37 (t, J=6.7 Hz, 2H), 4.30 (t, J=6.7 Hz, 2H), 2.01-1.94 (m, 4H), 1.62-1.57 (m, 4H), 1.49 (s, 12H), 1.40–1.28 (m, 24H), 0.91–0.87 (m, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ = 145.05, 143.79, 136.33, 134.03, 131.37, 130.71, 128.66, 127.93, 127.70, 125.73, 124.70, 122.88, 122.59, 119.61, 118.36. 83.85. 73.85. 73.81. 31.93. 30.63. 30.57. 29.70. 29.63. 29.59. 29.37, 26.34, 26.31, 25.06, 22.71, 14.13 ppm (only 15 of the 16 expected aromatic signals and only 15 of the 22 expected aliphatic signals observed); HRMS [APPI(+)], calcd for C₄₂H₆₁BO₄ ([M]⁺): 640.4669, found: 640.4716.

1,8-Diiodo-4,5-didecoxypyrene (21): To a solution of 4.5didecoxypyrene (8a) (2.00 g, 3.88 mmol) in CH₂Cl₂ (100 mL) was added iodine (2.96 g, 11.7 mmol) and $Hg(OAc)_2$ (3.71 g, 11.7 mmol). The reaction was stirred for 20 min at room temperature. The slurry was passed through short plug of silica gel and Celite[®] (ca. 1:1). Water (150 mL) was added and the layers were separated. The organic phase was dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The solid pink residue was subjected to column chromatography (10% CH₂Cl₂/hexanes) to yield 1,8-diiodo-4,5didecoxypyrene (21) (2.62 g, 88%) as a white solid. Rf (20% CH_2Cl_2 /hexanes) = 0.90; mp >95 °C dec.; ¹H NMR (CDCl₃, 300 MHz) δ = 8.53 (d, J=8.4 Hz, 2H), 8.35 (s, 2H), 8.21 (d, J=8.4 Hz, 2H), 4.30 (t, J=6.7 Hz, 4H), 2.02–1.86 (m, 4H), 1.65–1.50 (m, 4H), 1.42–1.23 (m, 24H), 0.95–0.81 (m, 6H); ¹³C NMR (75 MHz, CDCl₃): δ = 143.91, 137.47, $132.94,\ 132.40,\ 129.38,\ 123.13,\ \underline{121.31},\ 96.17,\ 73.90,\ 31.93,\ 30.52,$ 29.67, 29.61, 29.54, 29.36, 27.26, 22.70, 14.13; HRMS [APPI(+)], calcd for $C_{36}H_{48}I_2O_2$ ([M]⁺): 766.1744, found: 766.1757.

4,5-Didecoxy-1,8-bis(4,5-didecoxypyren-1-yl)pyrene (11a): *Method A (using dibromide* **17a)** – A 250 mL round-bottomed flask equipped with a side arm and capped with a rubber septum was charged with 2-(4,5-didecoxypyren-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**22**) (2.84 g, 4.46 mmol), 1,8-dibromo-4,5-didecoxypyrene (**17a**) (1.00 g, 1.49 mmol), anhydrous Ba(OH)₂ (5.09 g, 29.7 mmol), toluene (80 mL), ethanol (20 mL) and water (10 mL). The resulting slurry was subjected to three freeze-pump-thaw cycles before Pd(PPh₃)₄ (0.017 g, 0.015 mmol) was added under a positive pressure of N₂. The flask was then resealed with a rubber septum and heated at 80 °C in an oil bath for 24 h. After cooling to room temperature, the solvent was removed under reduced pressure and the resulting brown oil was dissolved in CH₂Cl₂ (2×100 mL). The

resulting solution was washed with H₂O (200 mL), dried over anhydrous MqSO₄ and the solvent was removed under reduced pressure to afford a yellow oil. The residue was subjected to column chromatography (1:1:10 toluene/CH₂Cl₂/hexanes) to yield 4,5-didecoxy-1,8-bis(4,5didecoxypyren-1-yl)pyrene (11a) (1.77 g, 77%) as a bright yellow viscous oil. R_f (7.5:7.5:85, toluene/CH₂Cl₂/hexanes) = 0.60; ¹H NMR (CDCl₃, 300 MHz) δ = 8.720 and 8.718 (2×d, J=8.1 Hz, 2H), 8.56 and 8.55 (2×d, J=8.1 Hz, 2H), 8.49 and 8.48 (2×dd, J=7.6, 1.5 Hz, 2H), 8.17 (d, J=8.1, 2H), 8.09 and 8.08 (2×d, J=8.1 Hz, 2H), 8.04 and 8.02 (2×dd, J=7.7, 1.3 Hz, 2H), 7.98 and 7.97 (2×t, J=7.6 Hz, 2H), 7.82 (d, J=9.3 Hz, 2H), 7.68 and 7.62 (2×d, J=9.2 Hz, 2H), 7.50 and 7.46 (2×s, 2H), 4.51 (t, J=6.7 Hz, 4H), 4.35 (m, 8H), 2.12-2.08 (m, 12H), 1.75-1.71 (m, 12H), 1.45-1.20 (m, 72H), 0.93–0.83 (m, 18H); 13 C NMR (CDCl₃, 75 MHz) δ = 144.43, 144.28, 144.25, 135.92, 135.91, 135.63, 135.60, 131.03, 130.15, 139.48, 129.42, 129.29, 139.27, 129.14, 129.12, 128.77, 127.61, 126.17, 125.80, 124.45, 123.47, 123.42, 123.19, 123.12, 119.79, 119.45, 119.37, 119.09, 119.00, 74.15, 73.99, 73.94, 32.14, 32.11, 30.94, 30.82, 29.96, 29.87, 29.80, 29.87, 29.80, 29.78, 29.60, 29.55, 26.63, 26.52, 22.91, 22.88, 14.31, 14.30, 14.28 ppm; HRMS [APPI(+)], calcd for C₁₀₈H₁₄₆O₆ ([M]⁺): 1539.1119, found: 1539.1109.

(23): 1,8-Bis(8-bromo-4,5-didecoxypyren-1-yl)-4,5-didecoxypyrene To a solution of 4.5-didecoxy-1.8-bis(4.5-didecoxypyren-1-yl)pyrene (11a) (0.050 g, 0.032 mmol) in CH₂Cl₂ (3 mL) was added a solution of bromine (0.010 g, 0.065 mmol) in CH₂Cl₂ (3 mL) and the reaction was stirred at room temperature for 5 min. Excess bromine was quenched by the addition of saturated sodium thiosulfate solution (5 mL). The layers were separated and the aqueous phase was extracted with CH₂Cl₂ (3×5 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The resulting brown solid was subjected to column chromatography (10% CH2Cl2/hexanes) to afford 1,8-bis(8-bromo-4,5-didecoxypyren-1-yl)-4,5didecoxypyrene (23) (0.043 g, 78%) as a pale yellow liquid. Rf (20% CH₂Cl₂/hexanes) = 0.38; ¹H NMR (CDCl₃, 300 MHz) δ = 8.740 and 8.738 (2×d, J=8.1 Hz, 2H), 8.609 and 8.606 (2×d, J=8.1 Hz, 2H), 8.33 and 8.32 (2×d, J=8.5 Hz, 2H), 8.24–8.10 (m, 8H), 7.80 and 7.74 (2×d, J=9.5 Hz, 2H), 7.49 and 7.45 (2×s, 2H), 4.52 (t, J=6.7 Hz, 4H), 4.39-4.29 (m, 8H), 2.17-2.04 (m, 4H), 2.01-1.89 (m, 8H), 1.78-1.66 (m, 4H), 1.66-1.17 (m, 80H), 0.94–0.78 (m, 18H); ¹³C NMR (75 MHz, CDCl₃): δ = 144.31, 144.15, 143.80, 136.09, 136.04, 135.35, 130.24, 129.94, 129.91, 129.59, 129.32, 129.24, 129.12, 128.77, 127.33, 127.29, 125.99, 125.89, 124.18, 123.23, 123.17, 122.46, 122.38, 120.36, 119.71, 119.49, 119.41, 74.09, 73.94, 73.92, 31.98, 31.94, 31.92, 30.77, 30.59, 29.79, 29.70, 29.63, 29.59, 29.43, 29.38, 26.46, 26.33, 22.75, 22.72, 22.70, 14.16, 14.14, 14.12; HRMS [APPI(+)], calcd for $C_{108}H_{144}^{\ 81}Br^{79}BrO_6$ ([M]⁺): 1697.9343, found: 1697.9330.

1,8-Bis(8-(4,5-didecoxypyren-1-yl)-4,5-didecoxypyren-1-yl)-4,5-

didecoxypyrene (13a): A 250 mL round-bottomed flask equipped with a side arm and capped with a rubber septum was charged with 2-(4,5-didecyloxypyren-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (22) (0.113 g, 0.117 mmol), 1,8-bis(8-bromo-4,5-didecoxypyren-1-yl)-4,5-didecoxypyrene (23) (0.100 g, 0.059 mmol), anhydrous Ba(OH)₂ (0.201 g, 1.18 mmol), toluene (16 mL), ethanol (4 mL) and water (2 mL). The resulting slurry was subjected to three freeze-pump-thaw cycles before Pd(PPh₃)₄ (0.007 g, 0.006 mmol) was added under a positive pressure of

N₂. The flask was then resealed with a rubber septum and heated at 80 °C in an oil bath for 24 h. After cooling to room temperature, the solvent was removed under reduced pressure and the resulting brown oil was dissolved in CH₂Cl₂ (2×35 mL). The resulting solution was washed with H₂O (50 mL), dried over anhydrous MgSO₄ and the solvent was removed under reduced pressure. The resulting yellow oil was subjected to column chromatography (1:1:10 toluene/CH₂Cl₂/hexanes) to afford 1,8-bis(8-(4,5-didecoxypyren-1-yl)-4,5-

didecoxypyrene (**13a**) (0.127 g, 84%) as a bright yellow viscous oil. $R_{\rm f}$ (7.5:7.5:85, toluene/CH₂Cl₂/hexanes) = 0.50; ¹H NMR (CDCl₃, 300 MHz) δ = 8.66–8.33 (m, 10H), 8.11–7.89 (m, 12H), 7.79–7.30 (m, 10H), 4.46–4.18 (m, 20H), 2.03–1.81 (m, 20H), 1.66–1.44 (m, 20H), 1.44–1.07 (m, 120H), 0.88–0.63 (m, 30H); ¹³C NMR (75 MHz, CDCl₃) δ 144.17, 144.11, 144.11, 135.50, 135.47, 130.87, 129.89, 129.87, 129.14, 128.89, 128.81, 128.57, 128.05, 127.41, 126.07, 126.02, 125.91, 125.83, 125.79, 125.72, 125.12, 124.54, 124.33, 124.30, 123.28, 123.26, 123.23, 123.17, 123.15, 122.93, 122.16, 121.78, 121.39, 120.36, 119.08, 118.99, 118.85, 77.46, 77.04, 76.62, 74.03, 74.00, 73.95, 73.92, 73.87, 31.96, 31.91, 30.73, 30.70, 30.67, 29.76, 29.74, 29.68, 29.67, 29.41, 29.36, 26.42, 26.37, 22.74, 14.16; HRMS [APPI(+)], calcd for C₁₈₀H₂₄₂O₁₀ ([M]⁺): 2563.8428, found: 2566.8658.

1,1'-Bi(4,5-didecoxypyrenyl) (10a): Method A (Suzuki-Miyaura crosscoupling) - A 250 mL round-bottomed flask equipped with a side arm and capped with a rubber septum was charged with 2-(4,5-didecoxypyren-1yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborylane (22) (1.46 g, 2.27 mmol), 1bromo-4,5-didecoxypyrene (20) (0.450 g, 0.758 mmol), anhydrous Ba(OH)₂ (2.60 g, 15.2 mmol), toluene (40 mL), ethanol (10 mL) and water (5 mL). The resulting slurry was subjected to three free-pump-thaw cycles before Pd(PPh₃)₄ (0.009 g, 0.008 mmol) was added under a positive pressure of N2. The flask was then resealed with a rubber septum and heated at 80 °C in an oil bath for 24 h. After cooling to room temperature, the solvent was removed under reduced pressure and the resulting brown oil was dissolved in CH₂Cl₂ (2×100 mL). The resulting solution was dried over anhydrous MgSO4 and the solvent was removed under reduced pressure to afford a vellow oil. The residue was subjected to column chromatography (1:1:10 toluene/CH2Cl2/hexanes) to afford 1,1'-bi(4,5-didecoxypyrenyl) (10a) (0.498 g, 64%) as a bright yellow viscous oil, which crystalized over 60 d. R_f (20% CH₂Cl₂/hexanes) = 0.35; ¹H NMR (CDCl₃, 300 MHz) δ = 8.66 (d, J=8.0 Hz, 2H), 8.55 (dd, J=7.5 Hz, 1.4 Hz 2H), 8.15 (d, J=8.0 Hz, 2H), 8.08 (d, J=7.2 Hz, 2H), 8.03 (t, J=7.7 Hz, 2H), 7.85 (d, J=9.3 Hz, 2H), 7.62 (d, J=9.3 Hz, 2H), 4.42 (m, 8H), 2.07–2.00 (m, 8H), 1.79–1.54 (m, 8H), 1.46–1.26 (m, 48H), 0.92–0.81 (m, 12H); ¹³C NMR (CDCl₃, 75 MHz) δ = 144.18, 135.62, 130.93, 130.07, 129.21, 128.98, 128.66, 127.47, 126.14, 125.75, 124.37, 123.00, 119.69, 118.99, 73.95, 73.90, 31.96, 31.94, 30.71, 30.68, 29.74, 29.66, 29.39, 26.39, 22.73, 22.71, 14.15, 14.13 ppm (only 14 of the 16 expected aromatic signals and only 14 of the 20 expected aliphatic signals observed); HRMS [APPI(+)], calcd for C₇₂H₉₈O₄ ([M]⁺): 1026.7465, found: 1026.7466.

Method B (Feringa homocoupling) – To a 2-necked pear-shaped flask equipped with a calcium chloride drying tube and a rubber septum was charged with 1-bromo-4,5-didecoxypyrene (**20**) (0.250 g, 0.421 mmol), *n*-hexane (5 mL), PEPPSI-iPrTM (0.003 g, 0.004 mmol) and the mixture was stirred at room temperature for 15 min. *t*-Butyllithium (0.3 M, 1.00 mL, 0.3 mmol) was then added dropwise over a period of 10 min through the rubber septum via syringe. The excess *t*-butyllithium was quenched by the addition of aqueous NH₄Cl solution (1 mL). The water and *n*-hexane were removed under reduced pressure and the resulting brown solid was dissolved in CH₂Cl₂ (15 mL) and passed through a plug of Celite and silica (ca. 1:1) The solvent was removed under reduced pressure to afford 4,5-didecoxyp-1-(4,5-didecoxypyren-1-yl)pyrene (**10a**) as a bright yellow viscous liquid (0.203 g, 94%).

Method C (Scholl reaction) – To a solution of 4,5-didecoxypyrene (**8a**) (0.100 g, 0.194 mmol) in CH_2Cl_2 (10 mL) and methanesulfonic acid (1 mL) was added DDQ (0.022 g, 0.097 mmol). The deep green solution was stirred at room temperature for 1 min and then quenched by the addition of aqueous 10% sodium bicarbonate solution (10 mL). The layers were separated and the organic phase was dried over anhydrous magnesium sulphate. The solvent was removed under reduced pressure and the resulting red solid was subjected to column chromatography (5% CH_2Cl_2 /hexanes) to afford 1,1'-bi(4,5-didecoxypyrenyl) (**10a**) as a bright yellow viscous oil (0.037 g, 37%) and 4,5-didecoxy-1,8-bis(4,5-didecoxypyren-1-yl)pyrene (**11a**) as a bright yellow viscous oil (0.017 g, 17%).

1,1'-Bi(8-bromo-4,5-didecoxypyrenyl) (24): To a solution of 1,1'-bi(4,5didecoxypyrenyl) (10a) (0.125 g, 0.122 mmol) in CH_2Cl_2 (10 mL) was added a solution of bromine (0.039 g, 0.24 mmol) in CH₂Cl₂ (10 mL) and the reaction was stirred at room temperature for 5 min. Excess bromine was guenched by the addition of saturated sodium thiosulfate solution (25 mL). The layers were separated and the aqueous phase was extracted with CH₂Cl₂ (3×25 mL). The organic phase was dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The resulting brown solid was subjected to column chromatography (10% CH2Cl2/hexanes) to afford 1,1'-bi(8-bromo-4,5didecoxypyrenyl) (24) (0.127 g, 88%) as a pale yellow solid. $R_{\rm f}$ (20% CH₂Cl₂/hexanes) = 0.60; mp=39.1-41.1 °C (crystallized from hexanes); ¹H NMR (CDCl₃, 300 MHz) δ = 8.70 (d, *J*=8.0 Hz, 2H), 8.40 (d, *J*=8.5 Hz, 2H), 8.27 (d, J=8.5 Hz, 2H), 8.23 (d, J=9.5 Hz, 2H), 8.17 (d, J=8.0 Hz, 2H), 7.73 (d, J=9.5 Hz, 2H), 4.43 (t, J = 6.7 Hz, 4H), 4.39 (t, J = 6.7 Hz, 4H), 2.08–1.96 (m, 8H), 1.72–1.59 (m, 8H), 1.50–1.24 (m, 48H), 0.93– 0.88 (m, 12H); ¹³C NMR (CDCl₃, 75 MHz) δ = 144.18, 143.90, 135.79, 130.36, 129.96, 129.56, 129.37, 128.97, 128.83, 127.21, 126.19, 124.21, 122.45, 120.49, 119.74, 119.56, 73.99, 31.96, 31.94, 30.67, 30.63, 29.73, 29.66, 29.63, 29.39, 26.37, 22.73, 22.71, 14.15, 14.13 ppm (only 14 of the 20 expected aliphatic signals observed); HRMS [APPI(+)], calcd for $C_{72}H_{96}^{81}Br^{79}BrO_4$ ([M]⁺): 1182.5675, found: 1182.5669.

1,1'-Bi(8-(4,5-didecoxypyrenyl)-4,5-didecoxypyrenyl (12a): A 250 mL round-bottomed flask equipped with a side arm and capped with a rubber septum was charged with 2-(4,5-didecyloxypyren-1-yl)-4,4,5,5tetramethyl-1,3,2-dioxaborolane (22) (0.227 g, 0.354 mmol), 1,1'-bi(8bromo-4,5-didecoxypyrenyl) (24) (0.140 g, 0.118 mmol), anhydrous Ba(OH)₂ (0.404 g, 2.36 mmol), toluene (16 mL), ethanol (4 mL) and water (2 mL). The resulting slurry was subjected to three freeze-pump-thaw cycles before Pd(PPh₃)₄ (0.014 g, 0.012 mmol) was added under a positive pressure of N2. The flask was then resealed with a rubber septum and heated at 80 °C in an oil bath for 24 h. After cooling to room temperature, the solvent was removed under reduced pressure and the resulting brown oil was dissolved in CH2Cl2 (2×35 mL). The resulting solution was washed with H₂O (50 mL), dried over anhydrous MgSO₄ and the solvent was removed under reduced pressure. The resulting yellow oil was subjected to column chromatography (1:1:10 toluene/CH2Cl2/hexanes) to afford 1,1'-bi(8-(4,5-didecoxypyrenyl)-4,5didecoxypyrenyl (12a) (0.172 g, 71%) as a bright yellow viscous oil. R_f (7.5:7.5:85, toluene/CH₂Cl₂/hexanes) = 0.55; ¹H NMR (CDCl₃, 300 MHz) δ = 8.70–8.46 (m, 8H), 8.16–7.94 (m, 10H), 7.86–7.40 (m, 8H), 4.51– 4.30 (m, 16H), 2.13-1.92 (m, 16H), 1.74-1.53 (m, 16H), 1.54-1.17 (m, 96H), 0.95–0.78 (m, 24H); ¹³C NMR (75 MHz, CDCl₃) δ = 144.21, 144.20, 144.15, 144.12, 135.65, 135.56, 135.53, 135.47, 130.89, 130.01, 129.89, 129.28, 129.15, 128.95, 128.87, 128.56, 127.45, 126.09, 126.05, 125.91, 125.88, 125.71, 124.34, 123.28, 123.20, 123.12, 122.99, 122.95, 119.66, 119.14, 118.94, 118.83, 74.01, 73.92, 73.89, 31.97, 30.73, 30.68, 29.75, 29.68, 29.42, 26.42, 26.39, 22.74, 14.16; HRMS [APPI(+)], calcd for $C_{144}H_{194}O_{8}\left(\left[M\right]^{*}\right):2051.4774,\,found:\,2051.4704.$

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FML?! Hardly a web-slang indictment of one's own existence! A new set of intensely fluorescent (ϕ =0.80) atropisomeric pyrene-based oligomers has been synthesized using a twostep iterative strategy. They have been shown to be room temperature liquids by POM, DSC and SWAXS analysis. As such, they join the growing family of *F*unctional *M*olecular *L*iquids. Delocalization in their excited states was found to be more extensive than in other pyrene-based systems.



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Synthesis of Oligo(1,8-pyrenylene)s – A Series of Functional Molecular Liquids