Synthesis and Characterization of Liquid Crystalline Perylene Diimides

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Several polyoxyethylene-substituted perylene-3,4,9,10-tetracarboxyldiimides have been synthesized and characterized. Relative to other known perylene diimide derivatives, all of the present compounds have much lower melting points and much greater solubility in common solvents. Most of these compounds possess liquid crystalline properties over a wide range of temperatures, some of them even at room temperature and below. Some of the photophysical and self-organizing characteristics of these compounds are demonstrated, particularly with regard to the spontaneous formation of a highly crystalline black phase. Generalized correlations about the physical properties and the chemical structures of these new liquid crystalline compounds are discussed. Their unusual physical and photophysical properties have important implications for their use in a variety of electroactive and photovoltaic applications.

Introduction

Liquid crystals (LCs) possess the remarkable ability to self-organize spontaneously into highly ordered structures that, when disturbed, simply reform the original structure. The ability to form large area, thin film, single crystals of electroactive materials would be of great importance for a number of applications.[1] However, most current LCs are electrical insulators and are used in applications such as flat panel displays. The recent advent of LC semiconductors[2−5] significantly expands the realm of potential applications for LCs. The use of LCs as active components in electroluminescent devices,[6] molecular wires and fibers,[7,8] and photorefractive materials[9,10] has been studied in the past few years. Furthermore, the photovoltaic properties of LC porphyrins have been investigated,[11,12] and the same materials have been proposed as a high-information-density optical storage medium.[13,14]

Perylene diimides, together with the parent compound perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA), represent one of the most thoroughly studied classes of organic semiconductors with possible applications in electrophotography, electroluminescent displays, and photovoltaic cells.[15−20] Perylene diimides are inexpensive, readily available, and robust compounds; the parent anhydride (PTCDA), for example, is a common component of automobile paint pigments. Moreover, perylene derivatives are highly fluorescent, and they exhibit singlet energy transfer over unusually long distances.[21] Several dioxotriazole derivatives of perylene that exhibited LC phases were reported recently,[22,23] but to our knowledge no report of LC derivatives of the more synthetically available and technologically useful perylene diimide core has appeared. A preliminary report of the spontaneous self-organization occurring in thin films of one such LC derivative, PPMEEM (**2e**), has been presented.[24] We report here the detailed synthesis and characterization of several liquid crystalline perylene

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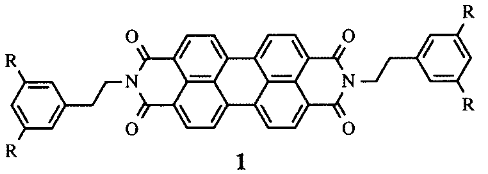
Scheme 1



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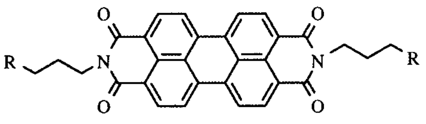
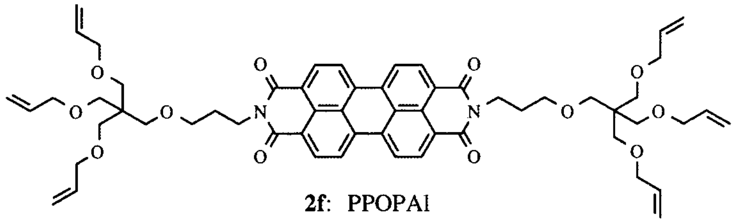


2

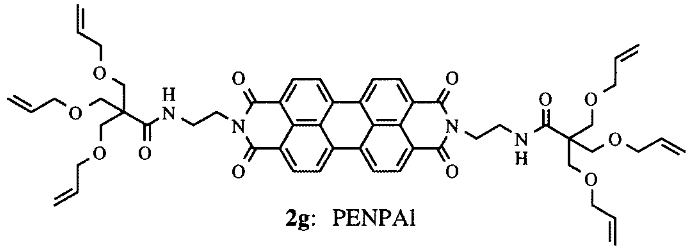
1a: PPEI (R = H)
1b: PPEIEEB (R = OEEB)
1c: PPEIEEEM (R = OEEEM)
1d: PPEIEEM (R = OEEM)

2a: PDDI (R = n-C_9H_{19})
2b: PPEEB (R = OEEB)
2c: PPEEEM (R = OEEEM)
2d: PPMEM (R = OMEM)
2e: PPMEEM (R = OMEEM)

EEB = $CH_2CH_2OCH_2CH_2OCH_2CH_2CH_2CH_3$
EEEM = $CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3$
EEM = $CH_2CH_2OCH_2CH_2OCH_3$
MEM = $CH[CH_2OCH_2CH_2OCH_3]_2$
MEEM = $CH[CH_2OCH_2CH_2OCH_2CH_2OCH_3]_2$



2f: PPOPAI



2g: PENPAI

diimides, and we describe some of their unique physical and photophysical properties. Although our interest in these compounds is primarily in their photovoltaic behaviors, their novel physical properties may also find applications in a number of other fields.

The new perylene diimide derivatives described here possess polyoxyethylene substituent groups. In preference to alkyl side chains, polyoxyethylene side chains were chosen as the means to induce liquid crystalline characteristics for several reasons: (1) their greater conformational flexibility should lead to lower clearing points (melting points); (2) their increased density should allow the perylene diimide aromatic cores to pack more tightly in order to maximize $\pi-\pi$ interactions; and (3) their increased polarity should promote wetting of substrate surfaces and also should allow for dissolution of dopants and ions in the side chain phase. For example, the presence of such polyoxyethylene substituents results in both a substantial decrease in melting point as well as a substantial increase in solubility with respect to the dodecyl-substituted imide (PDDI, **2a**) that lacks oxygen atoms in the side chain. The latter has a melting point greater than 325 °C and is appreciably soluble only in refluxing solvents such as chlorobenzene. Further generalizations and detailed discussions of the specific properties of the new liquid crystalline perylene diimides are presented below.

Results and Discussion

Syntheses. Liquid crystalline perylene diimides of two general structural types were synthesized, the structures of which are presented in Scheme 1. Derivatives of structure **1** were examined as extensions of earlier work concerning the parent phenethylimide (PPEI, **1a**). Examples of the second structural type, propylimide derivatives **2**, were prepared as conveniently available compounds whose physical and photovoltaic properties were to be compared with those of phenethylimide derivatives **1**.

As outlined in Scheme 2, the general synthesis of all LC perylene diimide structures **1** and **2** consisted of condensation of appropriately substituted primary amines **3** with an excess of commercially available perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA, **4**). Typical yields of isolated products were in the range 64–90%.

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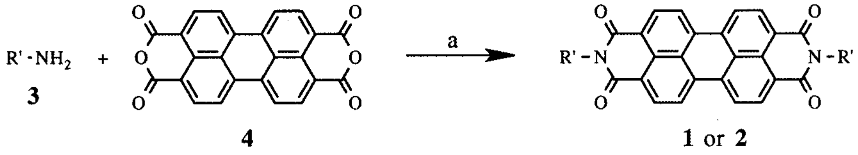
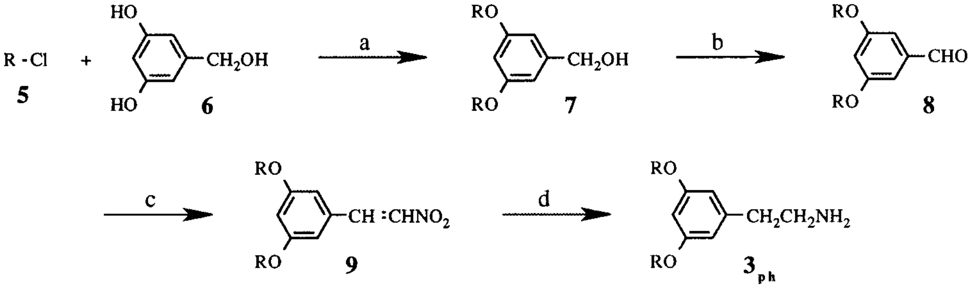
Scheme 2



(a) pyridine, 100-125 °C.

Scheme 3



b: R = EEB: $CH_2CH_2OCH_2CH_2OCH_2CH_2CH_2CH_3$
c: R = EEEM: $CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3$
d: R = EEM: $CH_2CH_2OCH_2CH_2OCH_3$

(a) NaOH / *n*-BuOH, reflux. (b) CrO_3 / pyridine / CH_2Cl_2, 25 °C. (c) CH_3NO_2 / NH_4OAc / HOAc, reflux. (d) $LiAlH_4$ / ether, reflux.

The synthetic methodology presented in Scheme 2 is a modification of conventional preparations of perylene diimide pigments.[17,25-27] Because of the greatly enhanced solubilities of the present perylene derivatives, it was found more convenient to conduct the condensation reactions in pyridine at more moderate temperatures (100–125 °C) rather than the conventional conditions involving refluxing quinoline or *N*-methyl-2-pyrrolidinone (NMP). Although longer reaction times were required in pyridine solution, product isolation was greatly facilitated because the more volatile solvent could be removed simply by evaporation. On the other hand, use of NMP as reaction solvent was complicated by the partial solubility of the LC perylenes **1** and **2** in water, which precluded the usual precipitation workup procedure.

The required primary amine precursors **3**$_{\mathbf{ph}}$ of phenethylimides **1** were prepared by two straightforward synthetic pathways from commercially available 3,5-dihydroxybenzyl alcohol (**6**). Both pathways began with formation of the polyoxyethylene-substituted alcohols **7**. The most reproducible preparations of **7** involved alkylation of the phenolic groups of **6** with appropriate alkyl chlorides **5**,[28] a procedure derived from reported preparations of polyoxyethylene derivatives of catechol and resorcinol.[29,30] The first synthetic pathway (Scheme 3) was based on a well-established synthetic route to phenethylamines involving β-nitrostyrene intermediates.[31,32] Thus, alcohols **7** were efficiently converted to aldehydes **8** by Collins oxidation.[33] Subsequent condensation with nitromethane afforded β-nitrostyrenes **9**, which were then reduced with lithium aluminum hydride[34] to yield the required phenethylamines **3**$_{\mathbf{ph}}$.

Scheme 3 worked well for preparation of amine precursors **3**$_{\mathbf{ph}}$**c** and **3**$_{\mathbf{ph}}$**d** of perylene diimides PPEIEEEM (**2c**) and PPEIEEM (**2d**), but it was quite unsatisfactory for producing amine precursor **3**$_{\mathbf{ph}}$**b** of PPEIEEB (**2b**) of reproducibly good quality. In fact, amine **3**$_{\mathbf{ph}}$**b** (R = EEB), inexplicably unlike amines **3**$_{\mathbf{ph}}$**c** and **3**$_{\mathbf{ph}}$**d** (R = EEEM and EEM, respectively), as prepared according to Scheme 3, was contaminated with varying amounts of unidentified impurities. These impurities could not be removed from the oily desired product by chromatography. Neither could they be removed by liquid–liquid extraction, because the corresponding hydrochloride salt was unexpectedly insoluble in water but very soluble in organic solvents such as methylene chloride and ether. Such unusual physical properties of the presently described compounds are quite unlike those of the readily recrystallized substances typically encountered by other researchers who have used the β-nitrostyrene route to phenethylamines.

Accordingly, an alternate synthetic pathway (Scheme 4) was developed that would be of general utility and also would avoid difficulties in purifying phenethylamines **3**$_{\mathbf{ph}}$. This unambiguous route was adapted from another known phenethylamine synthesis involving

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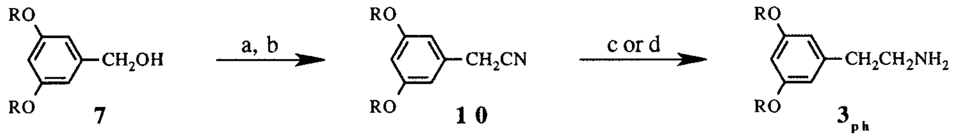
Scheme 4



b: R = EEB: $CH_2CH_2OCH_2CH_2OCH_2CH_2CH_2CH_3$
c: R = EEEM: $CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3$
d: R = EEM: $CH_2CH_2OCH_2CH_2OCH_3$

(a) $SOCl_2$ / pyridine / ether, 25 °C. (b) KCN / DMSO, 50 °C. (c) $NaBH_4$ / $CoCl_2$ / MeOH, 25 °C.
(d) H_2 / Raney Ni / NaOH / 95% EtOH

Scheme 5

$$\underset{\mathbf{11}}{ROH} + CH_2{=}CHCN \xrightarrow{a} \underset{\mathbf{12}}{ROCH_2CH_2CN} \xrightarrow{b} \underset{\mathbf{3_{pr}}}{ROCH_2CH_2CH_2NH_2}$$

b: R = EEB: $CH_2CH_2OCH_2CH_2OCH_2CH_2CH_2CH_3$
c: R = EEEM: $CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3$
d: R = MEM: $CH[CH_2OCH_2CH_2OCH_3]_2$
e: R = MEEM: $CH[CH_2OCH_2CH_2OCH_2CH_2OCH_3]_2$

(a) NaOMe (catalytic), 25 °C. (b) H_2 / Pt in EtOH / $CHCl_3$, 25 °C.

preparation and reduction of a nitrile intermediate, as accomplished, for example, by Baxter et al.[32] The alternate synthetic route is outlined in Scheme 4. Thus, polyoxyethylene-substituted alcohols **7** were very efficiently and without complication converted to nitriles **10** by way of the corresponding chlorides. Reduction of the nitriles **10**, however, was more problematic. Platinum-catalyzed hydrogenation[35] of **10**, for example, was extraordinarily slow compared to other nitriles (e.g., **12**) examined, and lithium aluminum hydride reduction[32,36] of **10** afforded amine products of very poor quality. However, two successful reduction methods were ultimately found. For example, sodium borohydride−cobaltous chloride[37,38] reduction of nitriles **10** was found to provide good yields of phenethylamines $\mathbf{3_{ph}}$. Although yields were sometimes disappointing, this reduction procedure had the advantage of producing a purified product in only a few hours. Much more efficient, although requiring longer reaction times, was a reduction procedure employing Raney-nickel catalyzed hydrogenation.[39] Overall, Scheme 4 is considered superior to Scheme 3 as a general synthesis of amines of type $\mathbf{3_{ph}}$. For example, amine precursor $\mathbf{3_{ph}b}$ (R = EEB) of perylene diimide **1b** (PPEIEEB) was prepared from the corresponding alcohol **7b** in 48% and 73% overall yield using the hydride reduction method and the hydrogenation reduction method, respectively. By contrast, Scheme 3, which afforded a 57% overall yield of precursor amine $\mathbf{3_{ph}c}$ (R = EEEM), appears to lack generality, because, as described above, $\mathbf{3_{ph}b}$ of acceptable quality could not be prepared. No difficulties of any kind were encountered using Scheme 4 for preparation of any of the presently described amines $\mathbf{3_{ph}}$. Scheme 4, therefore, should be considered the method of choice for convenient, efficient, and uncomplicated syntheses of any desired amines of type $\mathbf{3_{ph}}$ or any other related phenethylamine structure.

The required primary amine precursors $\mathbf{3_{pr}}$ of propylimides **2** were prepared as shown in Scheme 5. In this way, addition of appropriately substituted alcohols **11** to acrylonitrile occurred readily to give excellent yields of cyanoethylation[40] products **12**. On the basis of a reported catalytic hydrogenation method for preparation of amine hydrochlorides,[35] nitriles **12** were then reduced cleanly and very efficiently to the required amines $\mathbf{3_{pr}}$. Other attempted reduction procedures for preparation of amines $\mathbf{3_{pr}}$ were considerably less successful. Reductions of nitriles **12** with diborane,[41] for example, afforded very low yields, and sodium borohydride−cobaltous chloride[37,38] reductions either gave low yields or produced contaminated products that could not be purified effectively. In addition, lithium aluminum hydride reductions[36] of nitriles **12** resulted in apparent reversal of cyanoethylation, as reported for related aminonitriles,[37] because it was observed that most of the isolated reaction products consisted of alcohol starting materials **11**. The preparation of the precursor amine $\mathbf{3_{pr}f}$ (R = triallyl pentaerythrityl) of PPOPAl (**2f**) required special consideration because of the reducibility of the allyl substituent groups. As described in the Experimental Section, the latter lithium aluminum hydride reduction method was necessarily used in this case only to prepare a low but usable yield of amine $\mathbf{3_{pr}f}$.

Perylene diimide **2g** (PENPAl) was prepared in the usual way (Scheme 2) from amine **15**, which itself was

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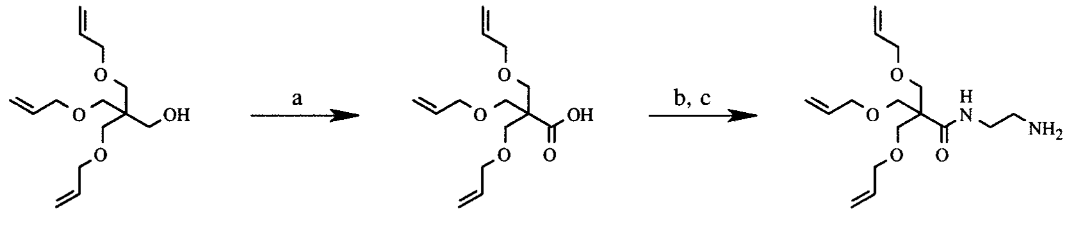
Scheme 6



13 **14** **15**

(a) Jones oxidation (b) $SOCl_2$ / DMF / CH_2Cl_2, 25 °C. (c) ethylenediamine / CH_2Cl_2, 25 °C.

synthesized from alcohol **13** according to the straightforward synthetic sequence presented in Scheme 6. It is noteworthy that the commercially available supply of triallyl compound **13** is only about 70% pure, the major contaminant being the corresponding diallyl ether. Conversion of this impurity to an acetonide derivative greatly facilitated a chromatographic separation, thus providing a convenient purification of triallyl ether **13**. As outlined in Scheme 6, purified alcohol **13** was oxidized to yield acid **14**, and conversion to amine **15** was ultimately accomplished by reaction of the corresponding acid chloride with ethylenediamine. Each of these transformations was uncomplicated, and the desired amine product **15** was obtained in very good overall yield.

The spectral characteristics (UV–vis, IR, NMR, MS) of all perylene diimides **1** and **2** (see Scheme 1) are fully in agreement with the structures shown. Complete spectral data for representative perylene compounds and ^{1}H NMR data for all perylene compounds may be found in the Experimental Section.

Liquid Crystalline Properties

Many of the perylene diimide structures described in Scheme 1 exhibited a liquid crystalline phase as evidenced by differential scanning calorimetry (DSC) as well as by observation of the optical textures on a polarizing microscope equipped with hot-stage. Calorimetric data for compounds **1**–**2** are presented in Table 1. In the table and in the following discussion, the symbols K, P_s, LC, and I refer to the crystalline solid, solidlike (either crystalline or high-viscosity LC), liquid crystalline, and isotropic liquid phases, respectively, of the compounds. Representative DSC traces of PPEEEM (**2c**), PPEIEEB (**1b**), and PPMEM (**2d**) are shown in Figures 1 and 2. DSC traces of PPMEEM (**2e**) were presented earlier.[24]

Table 1. Calorimetric Data for Compounds 1–2^a

compound^b	phase^c	T (ΔH)^d	phase	T (ΔH)	phase
PPEIEEB (**1b**)^{e,f}			LC	136 (8.2)	I
	P_s	34 (0.7)	LC	136 (8.0)	I
PPEIEEEM (**1c**)^f	P_s	20 (0.5)	LC	119 (2.0)	I
			LC	100 (6.9)	I
PPEIEEM (**1d**)^e			LC	169 (6.8)	I
			LC	169 (6.6)	I
PPEEB (**2b**)^f	K	73 (6.9)	LC	289 (5.9)	I
	K	66 (7.1)	LC	288 (5.6)	I
PPEEEM (**2c**)^f	K	122 (12.0)	LC	269 (4.7)	I
	K	67 (5.7)	LC	269 (4.0)	I
PPMEM (**2d**)^e	K	122 (14.1)	LC	167 (4.3)	I
	K	80 (8.7)	LC	167 (4.1)	I
PPMEEM (**2e**)^{e,g}	P_s	−43 (0.4)	LC	55 (15.4)	I
	P_s	−38 (2.0)	LC	59 (3.4)	I
PPOPAI (**2f**)^h			K	52 (2.0)	I
PENPAI (**2g**)^e			K	195 (5.5)	I
			K	194 (4.3)	I

[a] Heating and cooling rate 10 °C min^{-1}. Second entries are data obtained from the second heating scan. [b] See Scheme 1 for structures. [c] K = crystalline solid; P_s = solid-like phase, either crystalline or high viscosity LC; LC = liquid crystalline phase; I = isotropic liquid. [d] T, °C (ΔH, kcal mol^{-1}). [e] Exothermic transition observed. [f] Lesser endothermic transition(s) also observed. [g] Shapes of transition curves changed during subsequent heating. [h] No transitions observed during subsequent heating.

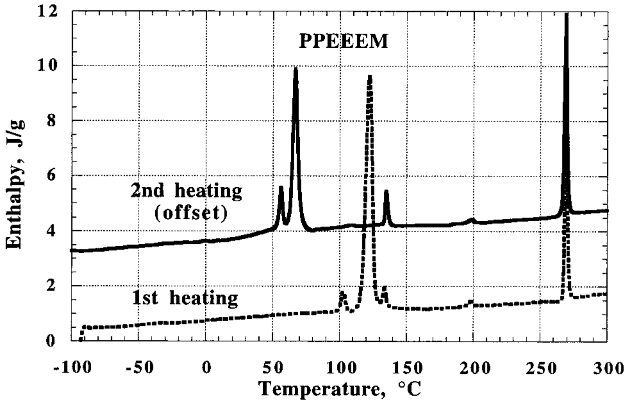


Figure 1. Differential scanning calorimeter traces of the first and second heatings of PPEEEM, **2c**. All subsequent scans closely matched the second scan. Scan rate was 10 °C per minute. Transition temperatures and enthalpies are given in Table 1.

The K → LC or P_s → LC transition temperatures for many of compounds **1**–**2** were observed to change substantially after the first heating of the original crystallized samples as illustrated in Figure 1 for **2c**. Accordingly, the DSC data in Table 1 include the results for two series of heating transitions: the first corresponds to melting of the crystals that were formed initially by solvent recrystallization during final purification of the samples; the second heating corresponds to melting the crystals that formed by cooling of the viscous, molten LC phase. Because crystallization from a viscous melt may not produce the same structures of the K and P_s phases as recrystallization from a solvent (polymorphism is very common in molecular crystals),[16] the transition temperatures and shapes may also change after first heating. No further changes were observed on subsequent scans, however. Therefore, for the discussion here, only the transitions observed for the second and subsequent heating scans will be considered.

Some of compounds **1**–**2** possess a liquid crystalline phase that exists over an unusually large temperature

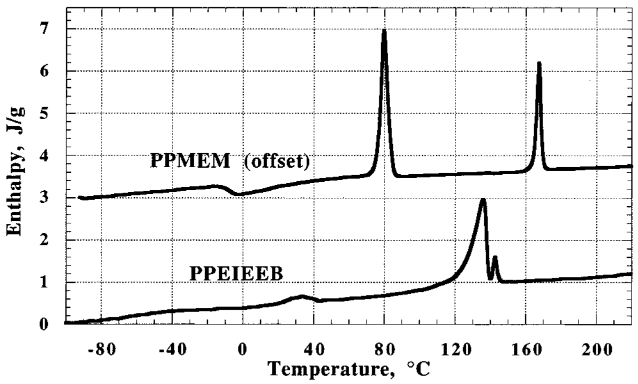


Figure 2. Differential scanning calorimeter traces of the second heatings of PPMEM (**2d**) and PPEIEEB (**1b**).

range; in the case of propylimide derivative **2b**, for example, it was observed to be approximately 220°. Similarly large LC ranges were also observed in the dioxotriazole derivatives of perylene[22,23] and may be a common feature of LCs based on the perylene core. The LC range may be similarly large for the phenethylimide derivatives, **1b**, **1c**, and **1d**, although the $P_s \rightarrow$ LC transitions for these compounds could not be observed in the microscope, and no definitive $P_s \rightarrow$ LC transitions could be assigned using the DSC. It is likely that this transition may be obscured by the high viscosity of the LC phase, even when cooling to below −100 °C. Upon cooling, the LC phases become extremely viscous, with the result that the molecules may freeze in the LC phase and be unable to crystallize on the time scale of our experiments. Such behavior is observed even in the case of **2e**, which is an LC at room temperature and has the most fluid LC phase of any compound described in Scheme 1: if an isotropic sample of **2e** is cooled rapidly to room temperature, it freezes into an apparently isotropic glassy state that crystallizes only slowly over a period of days. Thus, although compounds **1b**, **1c**, and **1d** are clearly identifiable in the microscope as liquid crystals below their clearing (LC → I) points, it was not possible to determine whether they were still LCs at room temperature. With the exception of compound **2e**, however, all of compounds **2** appeared to be crystalline solids at room temperature.

It is not yet clear what minimal structural features are required to produce compounds with an LC phase; however, the majority of the new compounds synthesized for this study did possess an LC phase. It is surprising that the addition of only two relatively short linear side chains (e.g., **2b** or **2c**) to a refractory crystalline compound like PTCDA is sufficient to induce liquid crystallinity. In contrast, for the cases of porphyrins and phthalocyanines that have aromatic cores slightly smaller and slightly larger, respectively, than PTCDA, eight side chains are usually required to induce liquid crystallinity. In the LC porphyrin, zinc octakis-(octylethyl ether)porphyrin (ZnOOEP), [5] for example, the ratio of side chain atoms (excluding hydrogens) to atoms in the aromatic core is 3.6, whereas in **2b** or **2c** this ratio is only 1.1. For electronic applications this is highly advantageous, because the benefits of liquid crystallinity may be achieved while keeping the volume of the electro-inactive side chain moiety to a minimum.

Physical and Photophysical Properties

Examination of the data in Table 1 leads to several generalizations concerning the physical properties of the LC perylenes described here. For example, consistent with the greater conformational mobility of ethers relative to alkanes, substitution of one oxygen atom for one methylene group (compare **1c** with **1b** and **2c** with **2b**) decreases the clearing point by approximately 20°. Also, from consideration of data for **2b** and **2c**, it appears that substitution of an oxygen atom for a methylene group results in a more narrow liquid crystalline range. The data in Table 1 clearly indicate that shortening of the side chains results in an increase in clearing point: eliminating one of the ethoxy units from the side chain increased the clearing point of **1d** by approximately 70° relative to **1c**; eliminating one ethoxy unit from each branch of the side chain increased the clearing point of **2d** by approximately 110° relative to **2e**. Whether the side chains are linear or branched also appears to affect the properties: compared to the linear chain derivatives **2b** and **2c**, the observed lower clearing points and lower viscosities of **2d** and **2e** may be a consequence of the branched chain of the glyceryl derivatives. For example, the branched side chain of **2d** contains only three atoms total more than the side chain of either **2b** or **2c**; however, its clearing point is more than 100° lower, although its liquid crystal range is considerably more narrow. Also, compound **2e**, which is unambiguously a liquid crystal at room temperature, is observed to be the least viscous of the LC perylenes described here, and it has an extraordinarily low clearing point. This effect of side chain branching may also account for the inability of pentaerythrityl derivatives **2f** and **2g** to form either an LC phase or a black phase (see below) in which there are strong electronic interactions between the perylene diimide cores. The highly branched tertiary carbons in these side chains may interfere with the regular and close packing required for liquid crystallinity and for formation of the black phase. The ability to form intermolecular hydrogen bonds in **2g** is most likely responsible for the large increase in melting point (140°) relative to **2f**.

As one example of the interesting physical and photophysical behavior of these novel perylene derivatives, Figure 3 shows a photomicrograph between crossed polarizers of an approximately 200 nm thick film of **2e** spin-coated onto an untreated glass microscope slide. Upon spin-coating from tetrahydrofuran (THF) solution, the film consisted of small (5−20 μm) randomly oriented crystallites. Over a period of about 48 h, the film spontaneously crystallized into the partially oriented, ribbonlike crystals shown in Figure 3. The film color changed from red to black during this self-ordering process, and the quantum yield for fluorescence increased by 7-fold.[24] These results indicate a spontaneous increase in the structural order of the film and a corresponding decrease in the concentration of exciton quenching sites. The spontaneous improvement in the structural and photophysical properties of the LC perylene film indicates that the highly ordered, highly emissive state is more thermodynamically stable than the originally formed state, and that there is a relatively low activation energy pathway leading to this preferred state. Similar spectroscopic changes occur in thermally evaporated films of PPEI (**1a**), but exposure to a solvent

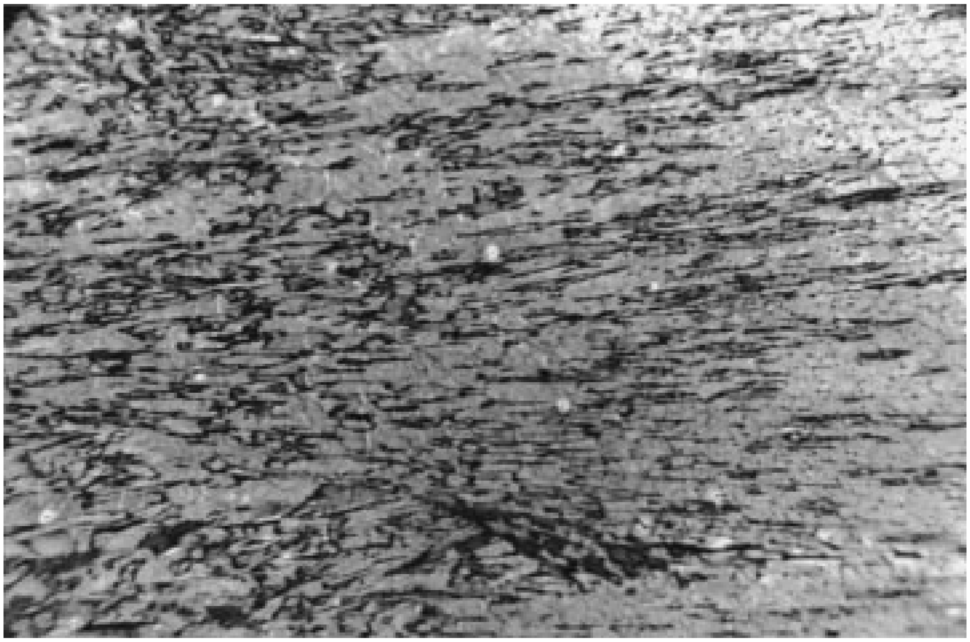


Figure 3. A photomicrograph of a 200 nm thick film of **2e** viewed between crossed polarizers. Area of the micrograph is 0.75 × 1.25 mm^2. This highly crystalline, partially oriented structure formed spontaneously within 48 h of spin-coating a solution of **2e** on an untreated microscope slide.[24] The original spin-coated film was red; the transformed structure shown here is black.

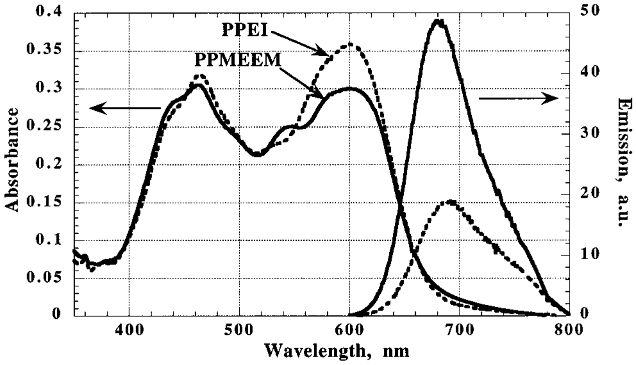


Figure 4. Absorption and fluorescence spectra of the film of PPMEEM, **2e**, shown in Figure 3 (solid lines) compared to a highly ordered film of polycrystalline PPEI, **1a**, (dashed lines). Excitation was at 518 nm for the fluorescence spectra; the spectra were corrected for the instrument response.

vapor such as methylene chloride is required to effect the transformation.[19] The crystallites grown during the solvent vapor annealing of PPEI films are too small to be seen in micrographs such as Figure 3 but have been visualized with scanning electron microscopy,[21] atomic force microscopy, and near-field scanning optical microscopy.[42] Films of **2e** spontaneously crystallize into structures hundreds of times larger than those occurring in PPEI films without the necessity of solvent vapor treatment. Perhaps more importantly, films of **2e** appear to maintain an approximately uniform physical contact to the substrate, in contrast to PPEI films that lose much of their physical and electrical contact to the substrates upon solvent vapor annealing.[21,42]

The absorption and fluorescence emission spectra of the film shown in Figure 3 of **2e** are presented in Figure 4 and compared to those of a highly ordered film of PPEI. The PPEI film was exposed to methylene chloride vapor for 41 h and consists of crystallites hundreds of nanometers in length. Both films are black and have similar absorption and emission spectra. However, the self-organized film of **2e** has a quantum yield for emission about 2.5 times larger than the already highly fluorescent PPEI. This suggests an even lower density of exciton recombination centers in the LC film and possibly a longer energy transfer length than in PPEI.[21] The width of the emission band (fwhm) also decreases slightly from 218 meV (1762 cm^{-1}) to 195 meV (1568 cm^{-1}) in the spin-coated **2e** film relative to the evaporated PPEI film, and the Stokes shift decreases by 30 meV. Taken together, these data suggest that the film of **2e** is more highly ordered than the PPEI film and may have superior electronic properties. The photophysical and photoelectrical properties of these new LC perylene derivatives will be described in more detail in future publications.

Conclusions

Several novel polyoxyethylene derivatives of perylene diimides have been synthesized and characterized by DSC and optical microscopy. Most of these compounds exhibited a liquid crystalline phase over a wide temperature range. Thin films of PPMEEM, a liquid crystal at room temperature, tend to self-organize spontaneously into a highly ordered crystalline phase that possesses photophysical properties superior to thermally evaporated, solvent vapor annealed films of the prototype perylene diimide, PPEI. The ability to form highly crystalline, highly fluorescent thin films spontaneously makes these new liquid crystalline semiconductors promising compounds for future studies.

Experimental Section

General Methods. Reagents of the highest quality available were obtained from commercial suppliers and used without further purification unless otherwise indicated. Commercially available reagent grade solvents were used as

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(42) Adams, D. M.; Kerimo, J.; Olson, E. J. C.; Zaban, A.; Gregg, B. A.; Barbara, P. F. *J. Am. Chem. Soc.* **1997**, *119*, 10608−10619.

obtained. Bond Elut silica extraction columns were obtained from Chrom Tech, Inc., Apple Valley, MN. ^{1}H NMR spectra (300 MHz) were recorded in $CDCl_3$ on a Varian Unity 300 spectrometer, all with tetramethylsilane as reference set to 0.0 ppm. ^{13}C NMR spectra (75 MHz) were recorded in $CDCl_3$ on a Varian Unity 300 spectrometer, all with $CDCl_3$ as reference set to 77.00 ppm. Electrospray ionization mass spectra (ESI-MS) were measured at the University of Colorado at Boulder on a Hewlett-Packard 5989B mass spectrometer equipped with a Hewlett-Packard 59987A ion source. All ESI-MS determinations were made in chloroform−methanol solution, and all protonated molecular ion isotopic patterns were consistent with expectation. Infrared spectra were recorded using a Nicolet 510P FT-IR spectrometer. UV−visible spectra were obtained using a Hewlett-Packard 8453 spectrophotometer. An SLM-Aminco AB2 spectrofluorometer equipped with a front-face cell holder was used to obtain emission spectra; the spectra were corrected for the instrument response. Differential scanning calorimetry (DSC) was performed with a TA Instruments DSC 2910. Optical textures were observed as a function of temperature between crossed polarizers on a Nikon polarizing microscope, equipped with a hot stage. Melting points were measured on a Laboratory Devices Mel-Temp apparatus and are reported uncorrected.

Representative Procedures for Scheme 2. General Preparation of Perylene Diimide Derivatives (1 and 2). Into a 50-mL pressure tube (Ace Glass #8648) equipped with a stirring bar were placed perylene-3,4,9,10-tetracarboxylic dianhydride (**4**) (0.50 g, 1.28 mmol), amine **3**$_{\mathbf{ph}}$ or **3**$_{\mathbf{pr}}$ (1.2−1.5 mmol), and pyridine (10 mL). The reaction mixture was sealed under a nitrogen atmosphere and heated with stirring in an oil bath at 100−110 °C. After 24 h, the resulting burgundy mixture was cooled, diluted with methylene chloride, and filtered through Celite to remove excess dianhydride. The filtrate was concentrated under reduced pressure, and the crude product was chromatographed directly on a silica extraction column: elution with methylene chloride removed colorless impurities; elution with 5% methanol in methylene chloride gave 64−90% yields of clean products. Final purifications were accomplished usually by recrystallization from methanol or 95% ethanol; low melting compound **2e** was purified by preparative thin layer chromatography on silica gel (5% methanol in methylene chloride eluent). All products were deep red in color, and most had a waxy texture.

Representative Procedures for Scheme 3. Synthesis of PPEIEEEM (1c). 2-[2-(2-Methoxyethoxy)ethoxy]ethyl Chloride (**5c**, R = EEEM). This compound was prepared by reaction of triethylene glycol monomethyl ether (Aldrich 31, 729-2) with thionyl chloride/pyridine in benzene according to the method of Pedersen:[28] 86% yield; bp 65−68° (0.1 Torr) [lit.[30] bp 112−113° (0.8 mm)]. IR (neat): 2877, 1456, 1353, 1300, 1249, 1200, 1105, 851, 666 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.39 (s, 3 H, OCH_3), 3.55−3.58 (m, 2 H, $\mathrm{OC}H_2$), 3.62−3.72 (m, 8 H, $\mathrm{OC}H_2$), 3.76 (br t, J = 6.0 Hz, 2 H, $\mathrm{ClC}H_2$).

*3,5-Bis[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]benzyl Alcohol (**7c**, R = EEEM).* A reaction mixture composed of 3,5-dihydroxybenzyl alcohol (**6**) (3.00 g, 21.4 mmol) and chloride **5c** (15.0 g, 82 mmol) in anhydrous methanol (200 mL) was prepared in a 500 mL round-bottomed flask equipped with a condenser, stirring bar, and gas inlet. Sodium methoxide (8.0 g, 148 mmol) was added in one portion, and the reaction mixture was refluxed with stirring under a nitrogen atmosphere. After 4 days, NMR analysis indicated incomplete conversion of the starting material but complete consumption of the excess chloride to form some of the desired product together with much triethylene glycol dimethyl ether (triglyme). Additional chloride **5c** (15 g) and sodium methoxide (8 g) were added, and the reaction was continued at reflux for 4 more days. After removing the solvent on a rotary evaporator, the oily residue was dissolved in water (300 mL), and the aqueous solution was extracted four times with methylene chloride. The combined extracts were dried (Na_2SO_4) and concentrated on a rotary evaporator. The residue was extracted several times with petroleum ether in order to remove remaining triglyme. The crude product was then chromatographed on silica gel (methylene chloride eluent) to yield the diether product cleanly as a pale yellow oil (6.29 g, 68%). IR (neat): 3451, 3056, 2877, 1597, 1450, 1351, 1299, 1172, 1126, 849, 734, 701 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.83 (br s, 1 H, $\mathrm{O}H$), 3.38 (s, 6 H, $\mathrm{C}H_3$), 3.54−3.57 (m, 4 H, $\mathrm{OC}H_2$), 3.64−3.76 (m, 16 H, $\mathrm{OC}H_2$), 3.84 (br t, J = 4.7 Hz, 4 H, $\mathrm{OC}H_2$), 4.11 (br t, J = 4.8 Hz, 4 H, $\mathrm{OC}H_2$), 4.61 (s, 2 H, $\mathrm{HOC}H_2$), 6.42 (t, J = 2.1 Hz, 1 H, Ar-H), 6.54 (d, J = 2.1 Hz, 2 H, Ar-H).

*3,5-Bis[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]benzaldehyde (**8c**, R = EEEM).* Anhydrous chromium trioxide (8.00 g, 80 mmol) was added in small portions over a period of 15 min to a vigorously stirred solution of pyridine (12.64 g, 160 mmol) in methylene chloride (150 mL). After the resulting burgundy-colored solution had been stirred at ambient temperature for 30 min, a solution of alcohol **7c** (3.50 g, 8.10 mmol) in methylene chloride (25 mL) was added at once. A tarry black deposit formed immediately, and stirring was continued at room temperature for an additional 30 min. The dark solution was decanted, and the tarry deposit was washed once with methylene chloride and twice with ether. The combined organic solutions were washed successively with four portions of 5% aq NaOH, four portions of 5% aq HCl, two portions of 5% aq $NaHCO_3$, and one portion of saturated brine. After drying (Na_2SO_4), the solvent was removed on a rotary evaporator. The residue was chromatographed on a silica extraction column (methylene chloride eluent) to yield 3.13 g (90%) of pure product as a pale yellow oil. IR (neat): 3085, 2877, 2731, 1698, 1594, 1450, 1390, 1350, 1299, 1249, 1177, 1110, 1069, 948, 851, 715, 678 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.38 (s, 6 H, $\mathrm{C}H_3$), 3.54−3.57 (m, 4 H, $\mathrm{OC}H_2$), 3.65−3.76 (m, 16 H, $\mathrm{OC}H_2$), 3.87 (br t, J = 4.8 Hz, 4 H, $\mathrm{OC}H_2$), 4.16 (br t, J = 4.8 Hz, 4 H, $\mathrm{OC}H_2$), 6.76 (t, J = 2.3 Hz, 1 H, Ar-H), 7.02 (d, J = 2.4 Hz, 2 H, Ar-H), 9.88 (s, 1 H, $\mathrm{C}H\mathrm{O}$).

*2-[3,5-Bis[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]phenyl]-1-ethanamine (**3**$_{\mathbf{ph}}$**c**, R = EEEM).* The following reaction mixture was prepared in a 50 mL round-bottomed flask equipped with a condenser, gas inlet, and stirring bar: aldehyde **8c** (2.80 g, 6.51 mmol), nitromethane (1.5 mL, 37 mmol), ammonium acetate (0.77 g, 10 mmol), and glacial acetic acid (15 mL). The reaction mixture was refluxed under a nitrogen atmosphere for 4 h. After cooling, the resulting dark mixture was diluted with water and extracted four times with methylene chloride. The combined extracts were washed with three portions of 5% aq $NaHCO_3$, dried with Na_2SO_4, and concentrated on a rotary evaporator. The light brown oily β-nitrostyrene **9c** obtained (2.90 g, 94%) was reduced in the following step without purification. IR (neat): 3091, 3057, 2878, 1595, 1517, 1448, 1338, 1297, 1178, 1109, 1070, 965, 850, 734, 697 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.38 (s, 6 H, $\mathrm{C}H_3$), 3.54−3.57 (m, 4 H, $\mathrm{OC}H_2$), 3.65−3.76 (m, 16 H, $\mathrm{OC}H_2$), 3.86 (br t, J = 4.8 Hz, 4 H, $\mathrm{OC}H_2$), 4.13 (br t, J = 4.8 Hz, 4 H, $\mathrm{OC}H_2$), 6.63 (t, J = 2.0 Hz, 1 H, Ar-H), 6.69 (d, J = 2.1 Hz, 2 H, Ar-H), 7.53 (d, J = 13.2 Hz, 1 H, $\mathrm{C{=}C}H$), 7.89 (d, J = 13.5 Hz, 1 H, $\mathrm{C{=}C}H$).

A mixture of lithium aluminum hydride (0.40 g, 10.5 mmol) in anhydrous THF (25 mL) was prepared in a 100 mL three-necked, round-bottomed flask equipped with a condenser, dropping funnel, stirring bar, and gas inlet. A solution of β-nitrostyrene **9c** (1.00 g, 2.11 mmol) in anhydrous THF (10 mL) was added dropwise with stirring over a period of 15 min. After refluxing with stirring for 2 h, the reaction mixture was hydrolyzed by successive addition with stirring and ice-cooling of 0.4 mL of water, 0.4 mL of 15% aq NaOH, and 1.2 mL of water. The resulting granular inorganic salts were removed by filtration and washed with methylene chloride. The combined organic solutions were dried (Na_2SO_4) and evaporated. The crude product was chromatographed on a silica extraction column (5% methanol in methylene chloride eluent) to yield 0.63 g (67% from **8c**) of pure amine as a slightly yellow viscous oil. IR (neat): 3356, 3066, 2875, 1675, 1595, 1450, 1351, 1296, 1172, 1109, 1072, 947, 849, 693 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.58 (br s, 2 H, $\mathrm{N}H_2$), 2.66 (t, J = 6.6 Hz, 2 H, $\mathrm{CH_2C}H_2\mathrm{NH_2}$), 2.94 (t, J = 6.8 Hz, 2 H, $\mathrm{C}H_2\mathrm{CH_2NH_2}$), 3.38 (s, 6 H, $\mathrm{C}H_3$), 3.54−3.57 (m, 4 H, $\mathrm{OC}H_2$), 3.64−3.76 (m, 16 H, $\mathrm{OC}H_2$), 3.84 (br t, J = 5.0 Hz, 4 H, $\mathrm{OC}H_2$), 4.09 (br t, J = 4.8

Hz, 4 H, OC*H*$_2$), 6.35 (t, *J* = 2.3 Hz, 1 H, Ar-*H*), 6.37 (d, *J* = 2.1 Hz, 2 H, Ar-*H*).

N,N′-Bis[2-[3,5-Bis[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]phenyl]ethyl]perylene-3,4,9,10-tetracarboxyldiimide (PPEIEEEM, ***1c****).* According to the general procedure above, this compound was obtained from amine $\mathbf{3_{ph}c}$ in 65% yield; mp 114−116°. IR (film): 2923, 2875, 1695, 1660, 1594, 1441, 1403, 1375, 1343, 1253, 1175, 1123, 852, 810, 748 cm^{-1}. ^{1}H NMR (CDCl$_3$): see below. ^{13}C NMR (CDCl$_3$): δ 34.51, 41.77, 59.04, 67.44, 69.71, 70.56, 70.66, 70.81, 71.93, 100.00, 107.78, 123.14, 123.22, 126.40, 129.32, 131.40, 134.62, 140.75, 159.98, 163.16. ESI-MS: 1247 (M$^+$); calcd for $C_{68}H_{82}N_2O_{20}$: 1246.5460.

Representative Procedures for Scheme 4. Synthesis of PPEIEEB (1b). *2-[2-(1-Butoxy)ethoxy]ethyl Chloride (****5b****, R = EEB).* This compound was prepared in 87% yield as described above for chloride **5c**: bp 56−58° (0.1 mm). IR (neat): 2959, 2934, 2869, 1458, 1355, 1299, 1119, 1053, 748, 668 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 0.92 (t, *J* = 7.2 Hz, 3 H, OCH$_2$CH$_2$CH$_2$C*H*$_3$), 1.37 (br sextet, *J* = 7.4 Hz, 2 H, OCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.57 (br quintet, *J* = 7.2 Hz, 2 H, OCH$_2$C*H*$_2$CH$_2$CH$_3$), 3.47 (t, *J* = 6.8 Hz, 2 H, OC*H*$_2$CH$_2$CH$_2$CH$_3$), 3.58−3.69 (m, 6 H, OC*H*$_2$), 3.77 (dt, *J* = 5.9, 0.7 Hz, 2 H, ClC*H*$_2$).

*3,5-Bis[2-[2-(1-butoxy)ethoxy]ethoxy]benzyl Alcohol (****7b****, R = EEB).* A reaction mixture composed of 3,5-dihydroxybenzyl alcohol (**6**) (3.50 g, 25.0 mmol), sodium hydroxide (1.00 g, 25.0 mmol), and 1-butanol (100 mL) was prepared in a 250 mL three-necked flask equipped with a condenser, dropping funnel, stirring bar, and gas inlet. The mixture was stirred and heated at reflux for the entire reaction period. After 1 h, chloride **5b** (4.50 g, 25.0 mmol) in 1-butanol (25 mL) was added dropwise over a period of 1 h. After an additional 1 h, more sodium hydroxide (1.00 g, 25.0 mmol) was added. After 30 min, another portion (4.50 g, 25.0 mmol) of chloride **5b** in 1-butanol (25 mL) was added dropwise over a period of 1 h. After 42 h, the resulting dark reaction mixture was cooled and filtered through Celite to remove a white solid. The filtrate was concentrated under reduced pressure. The resulting crude product was purified by chromatography on neutral alumina. Elution with methylene chloride removed unreacted chloride **5b** and a small amount of diethylene glycol dibutyl ether. Elution with 2% methanol in methylene chloride gave the product as a faintly yellow oil (7.32 g, 68% yield). IR (neat): 3431, 2958, 2933, 2871, 1597, 1450, 1353, 1295, 1246, 1171, 1124, 1071, 978, 843, 741 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 0.91 (t, *J* = 7.4 Hz, 6 H, OCH$_2$CH$_2$CH$_2$C*H*$_3$), 1.36 (br sextet, *J* = 7.4 Hz, 4 H, OCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.57 (br quintet, *J* = 7.1 Hz, 4 H, OCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.69 (br s, 1 H, O*H*), 3.47 (t, *J* = 6.8 Hz, 4 H, OC*H*$_2$CH$_2$CH$_2$CH$_3$), 3.59−3.62 (m, 4 H, OC*H*$_2$), 3.70−3.73 (m, 4 H, OC*H*$_2$), 3.85 (br t, *J* = 4.9 Hz, 4 H, OC*H*$_2$), 4.12 (br t, *J* = 4.8 Hz, 4 H, OC*H*$_2$), 4.61 (s, 2 H, HOC*H*$_2$), 6.42 (t, *J* = 2.3 Hz, 1 H, Ar-*H*), 6.54 (d, *J* = 2.4 Hz, 2 H, Ar-*H*).

*2-[3,5-Bis[2-[2-(1-butoxy)ethoxy]ethoxy]phenyl]ethanenitrile (****10b****, R = EEB).* A solution of thionyl chloride (4.0 mL, 55 mmol) in anhydrous ether (20 mL) was added dropwise with stirring during 30 min to a solution of alcohol **7b** (5.82 g, 13.6 mmol) in anhydrous ether (40 mL) containing pyridine (0.4 mL, 5 mmol). After the solution was stirred at room temperature for an additional 2 h, the resulting mixture was diluted with ether and washed three times with water. The organic layer was dried (Na$_2$SO$_4$) and evaporated to yield 5.75 g (95%) of chloride as a pale yellow oil. IR (neat): 2958, 2933, 2871, 1597, 1451, 1351, 1324, 1298, 1250, 1176, 1121, 1070, 845, 716 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 0.91 (t, *J* = 7.4 Hz, 6 H, OCH$_2$CH$_2$CH$_2$C*H*$_3$), 1.36 (br sextet, *J* = 7.3 Hz, 4 H, OCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.57 (br quintet, *J* = 7.3 Hz, 4 H, OCH$_2$C*H*$_2$CH$_2$CH$_3$), 3.47 (t, *J* = 6.8 Hz, 4 H, OC*H*$_2$CH$_2$CH$_2$CH$_3$), 3.59−3.62 (m, 4 H, OC*H*$_2$), 3.70−3.73 (m, 4 H, OC*H*$_2$), 3.85 (br t, *J* = 5.0 Hz, 4 H, OC*H*$_2$), 4.11 (br t, *J* = 5.0 Hz, 4 H, OC*H*$_2$), 4.49 (s, 2 H, ClC*H*$_2$), 6.45 (t, *J* = 2.4 Hz, 1 H, Ar-*H*), 6.55 (d, *J* = 2.4 Hz, 2 H, Ar-*H*).

A mixture of the above chloride and potassium cyanide (1.30 g, 20 mmol) in dimethylsulfoxide (40 mL) was stirred in an oil bath at 50−55° for 22 h. The resulting mixture was diluted with water and brine (to facilitate separation of layers) and extracted three times with ether. The combined extracts were washed with water, dried with Na$_2$SO$_4$, and evaporated. The residue was chromatographed on a silica extraction column (methylene chloride eluent) to yield 5.38 g (91% overall) of pale yellow oil. IR (neat): 2957, 2933, 2871, 2252, 1598, 1451, 1352, 1327, 1294, 1248, 1176, 1122, 1070, 838, 682 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 0.91 (t, *J* = 7.4 Hz, 6 H, OCH$_2$CH$_2$CH$_2$C*H*$_3$), 1.36 (br sextet, *J* = 7.3 Hz, 4 H, OCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.57 (br quintet, *J* = 7.2 Hz, 4 H, OCH$_2$C*H*$_2$CH$_2$CH$_3$), 3.47 (t, *J* = 6.8 Hz, 4 H, OC*H*$_2$CH$_2$CH$_2$CH$_3$), 3.59−3.62 (m, 4 H, OC*H*$_2$), 3.66 (s, 2 H, NCC*H*$_2$), 3.70−3.73 (m, 4 H, OC*H*$_2$), 3.85 (br t, *J* = 4.7 Hz, 4 H, OC*H*$_2$), 4.11 (br t, *J* = 4.8 Hz, 4 H, OC*H*$_2$), 6.45 (t, *J* = 2.1 Hz, 1 H, Ar-*H*), 6.47 (d, *J* = 2.1 Hz, 2 H, Ar-*H*).

2-[3,5-Bis[2-[2-(1-butoxy)ethoxy]ethoxy]phenyl]-1-ethanamine ($\mathbf{3_{ph}b}$*, R = EEB). Method a.* A solution of nitrile **10b** (2.06 g, 4.71 mmol) and cobalt(II) chloride hexahydrate (2.38 g, 10 mmol) in methanol (50 mL) was placed in a water bath at 10−15 ° C. Sodium borohydride (3.80 g, 100 mmol) was added in portions during 10 min (exothermic gas evolution). The resulting black reaction mixture was stirred at room temperature for 2.5 h and then cautiously acidified with concentrated hydrochloric acid (20 mL). The solvent was removed on a rotary evaporator, and the blue solid was treated with concentrated ammonia (50 mL). The resulting mixture was extracted three times with methylene chloride. After the mixture was dried (Na$_2$SO$_4$), the combined extracts were evaporated to yield a gray viscous oil. Chromatography on a silica extraction column (eluent 5% methanol in methylene chloride) removed an unidentified impurity (0.45 g), which was followed by 1.11 g (53%) of the pure amine (eluent 10−20% methanol in methylene chloride). IR (neat): 3371, 2957, 2932, 2870, 1594, 1451, 1352, 1293, 1247, 1173, 1125, 1072, 840, 698 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 0.91 (t, *J* = 7.4 Hz, 6 H, OCH$_2$CH$_2$CH$_2$C*H*$_3$), 1.36 (br sextet, *J* = 7.4 Hz, 4 H, OCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.57 (br quintet, *J* = 7.2 Hz, 4 H, OCH$_2$C*H*$_2$CH$_2$CH$_3$), 2.47 (br s, 2 H, N*H*$_2$), 2.77 (t, *J* = 6.8 Hz, 2 H, CH$_2$C*H*$_2$NH$_2$), 3.02 (t, *J* = 7.0 Hz, 2 H, C*H*$_2$CH$_2$NH$_2$), 3.47 (t, *J* = 6.8 Hz, 4 H, OC*H*$_2$CH$_2$CH$_2$CH$_3$), 3.59−3.62 (m, 4 H, OC*H*$_2$), 3.69−3.72 (m, 4 H, OC*H*$_2$), 3.84 (br t, *J* = 4.8 Hz, 4 H, OC*H*$_2$), 4.09 (br t, *J* = 4.7 Hz, 4 H, OC*H*$_2$), 6.36 (t, *J* = 2.1 Hz, 1 H, Ar-*H*), 6.39 (d, *J* = 2.1 Hz, 2 H, Ar-*H*).

Method b. A solution of nitrile **10b** (4.37 g, 10 mmol) in 25 mL of 1.4 M sodium hydroxide in 95% ethanol was prepared in a 100 mL Fisher-Porter reactor equipped with a stirring bar. Raney-nickel slurry (0.5 g, Aldrich 22,167-8) was added, and the reactor was pressurized with hydrogen gas. The reaction mixture was stirred at room temperature for 44 h while maintaining an internal pressure of approximately 50 psi. The resulting mixture was filtered through Celite, the catalyst washed with 95% ethanol, and the filtrate concentrated on a rotary evaporator. The residue was mixed with water and extracted three times with ether. The combined extracts were dried (Na$_2$SO$_4$) and evaporated. The resulting crude product was chromatographed on a silica extraction column: elution with methylene chloride removed a small amount of unidentified impurity; continued elution with 5−10% methanol in methylene chloride provided 3.52 g (80%) of pure amine $\mathbf{3_{ph}b}$ as a faintly yellow viscous oil.

N,N′-Bis[2-[3,5-Bis[2-[2-(1-butoxy)ethoxy]ethoxy]phenyl]ethyl]perylene-3,4,9,10-tetracarboxyldiimide (PPEIEEB, ***1b****).* Reaction of amine $\mathbf{3_{ph}b}$ with perylene anhydride **4** in pyridine as described in the general procedure above afforded a 65% yield; mp 135−137°. IR (neat): 2958, 2933, 2867, 1696, 1657, 1594, 1440, 1404, 1341, 1322, 1277, 1254, 1177, 1128, 1075, 1005, 850, 832, 809, 748 cm^{-1}. ^{1}H NMR (CDCl$_3$): see below. ^{13}C NMR (CDCl$_3$): δ 13.94, 19.28, 31.71, 34.50, 41.78, 67.46, 69.71, 70.11, 70.85, 71.26, 99.98, 107.78, 123.11, 123.21, 126.36, 129.29, 131.37, 134.58, 140.73, 159.99, 163.13. ESI-MS: 1239 (M$^+$); calcd for $C_{72}H_{90}N_2O_{16}$: 1238.6290.

Representative Procedures for Scheme 5. Synthesis of PPMEM (2d). *1,3-Bis(2-methoxyethoxy)-2-propanol (****11d****, R = MEM).* On the basis of the reported synthesis[43] of 1,3-bis[2-(2-methoxyethoxy)ethoxy]-2-propanol, alcohol **11d** was

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[43] Vacus, J.; Simon, J. *Adv. Mater.* **1995**, *7*, 797−800.

prepared in 61% yield by reaction of the sodium derivative of ethylene glycol monomethyl ether with epichlorohydrin; bp 90−93 (0.4 Torr). IR (neat): 3446, 2875, 1456, 1362, 1286, 1246, 1200, 1109, 1046, 849 cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 2.94 (br s, 1 H, $\mathrm{O}H$), 3.39 (s, 6 H, $\mathrm{OC}H_3$), 3.49−3.61 (m, 8 H, $\mathrm{C}H_2\mathrm{CHOH}$ and $\mathrm{C}H_2\mathrm{O}$), 3.65−3.68 (m, 4 H, $\mathrm{C}H_2\mathrm{O}$), 3.98−4.05 (m, 1 H, $\mathrm{C}H\mathrm{OH}$).

*3-[1,3-Bis(2-methoxyethoxy)-2-propoxy]propanenitrile (**12d**, R = MEM).* Sodium methoxide (50 mg, 1 mmol) was added in one portion to a stirred reaction mixture composed of 1,3-bis(2-methoxyethoxy)-2-propanol **(11d)** (5.0 g, 24 mmol) and acrylonitrile (5.0 mL, 4.0 g, 76 mmol) under a nitrogen atmosphere. The reaction mixture warmed quickly to about 50° and then cooled slowly as the reaction proceeded at ambient temperature for 14 h. The resulting yellow mixture consisted of a large amount of suspended solid. A 0.2 mL portion of acetic acid was added, and the excess acrylonitrile was removed at reduced pressure. The residual oily solid was suspended in methylene chloride and filtered through Celite, and the filtrate evaporated. The crude product was chromatographed on a silica extraction column (methylene chloride eluent) to yield 5.85 g (93%) of slightly yellow oil, which was used without further purification. IR (neat): 2880, 2250, 1456, 1362, 1286, 1246, 1200, 1109, 1029, 850 cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 2.62 (t, J = 6.5 Hz, 2 H, $\mathrm{OCH_2C}H_2\mathrm{CN}$), 3.38 (s, 6 H, $\mathrm{OC}H_3$), 3.51−3.65 (m, 12 H, $\mathrm{C}H_2\mathrm{C}H_2\mathrm{OC}H_2$), 3.70−3.77 (m, 1 H, $\mathrm{OCH_2C}H\mathrm{O}$), 3.88 (t, J = 6.6 Hz, 2 H, $\mathrm{OC}H_2\mathrm{CH_2CN}$).

*3-[1,3-Bis(2-methoxyethoxy)-2-propoxy]-1-propanamine (**3$_{pr}$d**, R = MEM).* Into a 250 mL Fisher-Porter reactor equipped with a stirring bar were placed nitrile **12d** (1.05 g, 4.02 mmol), platinum oxide (100 mg), chloroform (2 mL), and absolute ethanol (100 mL). The reactor was pressurized with hydrogen gas, and the reaction mixture was stirred at room temperature overnight (15 h) while maintaining an internal pressure of approximately 50 psi. Potassium carbonate (4 g) was then added, and the mixture was stirred at room temperature for 2 h. The resulting mixture was filtered through Celite, and the filtrate was concentrated on a rotary evaporator. The crude product was chromatographed on a silica extraction column: elution with methylene chloride removed a small amount of unidentified impurity, and continued elution with 10−25% methanol in methylene chloride provided 0.80 g (75%) of pure amine product as a faintly yellow oil. IR (neat): 3364, 2875, 1457, 1361, 1246, 1199, 1108, 1029, 985, 850 cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.52 (br s, 2 H, $\mathrm{N}H_2$), 1.71 (quintet, J = 6.3 Hz, 2 H, $\mathrm{OCH_2C}H_2\mathrm{CH_2NH_2}$), 2.80 (t, J = 6.7 Hz, 2 H, $\mathrm{OCH_2CH_2C}H_2\mathrm{NH_2}$), 3.38 (s, 6 H, $\mathrm{OC}H_3$), 3.47−3.65 (m, 13 H, $\mathrm{C}H_2\mathrm{C}H_2\mathrm{OC}H_2\mathrm{C}H$), 3.68 (t, J = 6.2 Hz, 2 H, $\mathrm{OC}H_2\mathrm{CH_2CH_2NH_2}$).

*N,N′-Bis[3-[1,3-bis(2-methoxyethoxy)-2-propoxy]propyl]perylene-3,4,9,10-tetracarboxyldiimide (PPMEM, **2d**).* As described in the general procedure above, this compound was synthesized from amine **3$_{pr}$d** in 90% yield and obtained as fine cottony waxy crystals; mp 162−164°. IR (neat): 2923, 2874, 1697, 1655, 1595, 1443, 1403, 1356, 1250, 1178, 1110, 858, 811, 745 cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): see below. ^{13}C NMR ($\mathrm{CDCl_3}$): δ 28.74, 38.22, 59.01, 68.46, 70.76, 71.33, 71.90, 78.00, 122.89, 123.20, 126.14, 129.13, 131.14, 134.29, 163.15. ESI-MS: 886 (M$^+$); calcd for $\mathrm{C_{48}H_{58}N_2O_{14}}$: 886.3888.

Procedures for Scheme 6. *2,2,2-Tris(allyloxymethyl)ethanol (Pentaerythritol Triallyl Ether) (13).* The commercially available material (Aldrich 25,172-0) is only about 70% pure, the major contaminant being the diallyl ether. The following conversion of this impurity to an acetonide derivative provides a convenient means for removing this impurity and thereby obtaining the pure triallyl ether.

A reaction vessel was assembled from a 100 mL round-bottomed flask, a 15 cm vacuum-jacketed column packed with glass beads, and a short-path stillhead. The reaction flask was charged with pentaerythritol triallyl ether (20 g, approx 70% pure, Aldrich 25,172-0), dimethoxypropane (3.00 g, 28.7 mmol), *p*-toluenesulfonic acid (20 mg), and benzene (40 mL). The reaction mixture was heated to boiling, and the methanol−benzene azeotrope distilled at about 53°, after which the head temperature rose to about 75° as benzene distilled. Approximately 40 mL total of distillate was collected after 45 min. Remaining volatile material was removed under reduced pressure. The residue was chromatographed on alumina: elution with methylene chloride afforded 8.58 g of a mixture of acetonides and tetraallyl ether; elution with 5% methanol in methylene chloride yielded 10.97 g of pure triallyl ether. IR (neat): 3469, 3080, 3014, 2980, 2866, 1647, 1479, 1421, 1351, 1266, 1138, 1090, 1048, 993, 924 cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 2.91 (t, J = 6.1 Hz, 1 H, $\mathrm{O}H$), 3.50 (s, 6 H, $\mathrm{OC}H_2$), 3.74 (d, J = 6.0 Hz, 2 H, $\mathrm{C}H_2\mathrm{OH}$), 3.96 (dt, J = 5.7, 1.5 Hz, 6 H, $\mathrm{CH_2{=}CHC}H_2$), 5.17 (dq, J = 10.5, 1.2 Hz, 3 H, $\mathrm{C}H_2\mathrm{{=}CHCH_2}$), 5.25 (dq, J = 17.1, 1.7 Hz, 3 H, $\mathrm{C}H_2\mathrm{{=}CHCH_2}$), 5.81−5.94 (m, 3 H, $\mathrm{CH_2{=}C}H\mathrm{CH_2}$).

*2,2,2-Tris(allyloxymethyl)acetic Acid (**14**).* A reaction mixture consisting of purified alcohol **13** (2.68 g, 10.5 mmol) in reagent grade acetone (20 mL) was cooled in an ice−water bath. Jones reagent[44] (16 mL, approximately 30 mmol) was added dropwise with stirring over a period of 15 min. The cooling bath was removed, and stirring was continued at room temperature overnight (21 h). The resulting green reaction mixture was diluted with water and extracted three times with ether. The combined ether solutions were washed with water and extracted three times with 5% aq $\mathrm{NaHCO_3}$. The combined extracts were washed with ether, cooled in ice−water, and cautiously acidified with concentrated HCl. The resulting cloudy mixture was extracted three times with ether, and the combined ether extracts were dried ($\mathrm{Na_2SO_4}$) and concentrated on a rotary evaporator to yield 1.74 g (61%) of colorless oil. This material was sufficiently pure for use directly in the following step. IR (neat): 3080, 3015, 2918, 2875, 1712, 1647, 1478, 1422, 1351, 1251, 1136, 1090, 990, 925 cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 3.68 (s, 6 H, $\mathrm{OC}H_2$), 4.01 (br d, J = 5.4 Hz, 6 H, $\mathrm{CH_2{=}CHC}H_2$), 5.18 (dd, J = 10.5, 0.9 Hz, 3 H, $\mathrm{C}H_2\mathrm{{=}CHCH_2}$), 5.26 (dd, J = 17.1, 1.6 Hz, 3 H, $\mathrm{C}H_2\mathrm{{=}CHCH_2}$), 5.80−5.93 (m, 3 H, $\mathrm{CH_2{=}C}H\mathrm{CH_2}$), 11.26 (s, 1 H, $\mathrm{COO}H$).

*2-[2,2,2-Tris(allyloxymethyl)acetamido]-1-ethanamine (**15**).* The following acid chloride preparation is based on known procedures.[45,46] A 2.5 mL (5.0 mmol) portion of 2 M thionyl chloride in methylene chloride was added to acid **14** (0.68 g, 2.5 mmol) dissolved in methylene chloride (15 mL) containing two drops of dimethylformamide. After the reaction mixture was stirred at room temperature for 45 min, the solvent was removed at reduced pressure. Residual thionyl chloride was removed by adding benzene (10 mL) and evaporating under reduced pressure to yield 0.71 g (98%) of yellow oil. IR (neat): 3082, 3015, 2981, 2922, 2877, 2857, 1794, 1647, 1480, 1422, 1350, 1265, 1138, 1090, 988, 918, 840, 676 cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 3.68 (s, 6 H, $\mathrm{OC}H_2$), 4.00 (dt, J = 5.5, 1.5 Hz, 6 H, $\mathrm{CH_2{=}CHC}H_2$), 5.18 (dq, J = 10.4, 1.5 Hz, 3 H, $\mathrm{C}H_2\mathrm{{=}CHCH_2}$), 5.26 (dq, J = 17.3, 1.6 Hz, 3 H, $\mathrm{C}H_2\mathrm{{=}CHCH_2}$), 5.80−5.93 (m, 3 H, $\mathrm{CH_2{=}C}H\mathrm{CH_2}$).

The above crude acid chloride in methylene chloride (15 mL) was added dropwise with stirring during 15 min to ethylenediamine (2 mL, ~30 mmol) in methylene chloride (10 mL). After the solution was stirred at room temperature for 2 h, the reaction mixture was extracted with three portions of 5% aq HCl. The combined acid extracts were washed with methylene chloride and made basic with solid NaOH. The resulting mixture was extracted with three portions of methylene chloride, and the combined extracts were dried ($\mathrm{Na_2SO_4}$) and evaporated. After chromatography on a silica extraction column (5% methanol in methylene chloride eluent), there was obtained 0.60 g (77% from acid **14**) of faintly yellow viscous oil. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.34 (br s, 2 H, $\mathrm{N}H_2$, exchanged with $\mathrm{D_2O}$), 2.79 (t, J = 6.0 Hz, 2 H, $\mathrm{CH_2C}H_2\mathrm{NH_2}$), 3.31 (q, J = 5.8 Hz, 2 H, $\mathrm{C}H_2\mathrm{CH_2NH_2}$, reduced to t with $\mathrm{D_2O}$), 3.70 (s, 6 H, $\mathrm{OC}H_2$), 3.99 (dt, J = 5.4, 1.4 Hz, 6 H, $\mathrm{CH_2{=}CHC}H_2$), 5.17 (dq, J = 10.3, 1.4 Hz, 3 H, $\mathrm{C}H_2\mathrm{{=}CHCH_2}$), 5.26 (dq, J = 17.3, 1.6

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[44] Meinwald, J.; Crandall, J.; Hymans, W. E. *Org. Synth. Coll. Vol. V* **1973**, 866−868.

[45] Bosshard, H. H.; Mory, R.; Schmid, M.; Zollinger, H. *Helv. Chim. Acta* **1959**, *42*, 1653.

[46] Egawa, Y.; Suzuki, M.; Okuda, T. *Chem. Pharm. Bull.* **1963**, *11*, 589.

Hz, 3 H, $\mathrm{C}H_2\mathrm{{=}CHCH_2}$), 5.82−5.95 (m, 3 H, $\mathrm{CH_2{=}C}H\mathrm{CH_2}$), 7.25 (br s, 1 H, $\mathrm{CON}H$, exchanged with $\mathrm{D_2O}$).

3-[2,2,2-Tris(allyloxymethyl)ethoxy]-1-propanamine ($\mathbf{3}_{\mathbf{pr}}\boldsymbol{f}$). A mixture of lithium aluminum hydride (0.40 g, 10.5 mmol) in anhydrous ether (40 mL) was prepared in a 100 mL three-necked round-bottomed flask equipped with a condenser, dropping funnel, stirring bar, and gas inlet. After this suspension was stirred overnight at room temperature under a nitrogen atmosphere, nitrile **12g** (3.00 g, 9.71 mmol) in anhydrous ether (25 mL) was added dropwise with stirring and ice-cooling over a period of 45 min. The reaction mixture was heated at reflux with stirring for 2 h. The mixture was then hydrolyzed by successive addition with stirring and ice-cooling of 0.4 mL of water, 0.4 mL of 15% aq NaOH, and 1.2 mL of water. The resulting granular inorganic salts were removed by filtration and washed with ether. The combined ether solutions were extracted four times with 5% aq HCl, and the acidic extracts were washed with two portions of ether. The combined ether solutions were dried ($\mathrm{Na_2SO_4}$) and evaporated to yield 1.57 g (6.13 mmol, 63%) of a slightly yellow oil, which was identified (NMR) as triallyl ether **13**.

The above acid extracts were cooled in ice−water, made basic with solid NaOH, and extracted four times with ether. After drying ($\mathrm{Na_2SO_4}$), the ether was evaporated to yield a slightly yellow oil (0.94 g, 31% yield, 84% conversion). Although sufficiently pure for use directly, the amine product may be purified further by column chromatography on silica gel (5% methanol in methylene chloride eluent). IR (neat): 3370, 3305, 3079, 3014, 2911, 2868, 1646, 1479, 1421, 1350, 1267, 1172, 1095, 992, 923 cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.11 (br s, 2 H, $\mathrm{N}H_2$), 1.68 (quintet, $J = 6.3$ Hz, 2 H, $\mathrm{CH_2C}H_2\mathrm{CH_2NH_2}$), 2.78 (t, $J = 6.8$ Hz, 2 H, $\mathrm{CH_2CH_2C}H_2\mathrm{NH_2}$), 3.42 (s, 2 H, $\mathrm{C}H_2\mathrm{OCH_2CH_2CH_2NH_2}$), 3.44 (s, 6 H, $\mathrm{C}H_2\mathrm{O}$), 3.47 (t, $J = 6.0$ Hz, 2 H, $\mathrm{C}H_2\mathrm{CH_2CH_2NH_2}$), 3.95 (dt, $J = 5.4$, 1.7 Hz, 6 H, $\mathrm{CH_2{=}CHC}H_2$), 5.13 (dq, $J = 10.4$, 1.5 Hz, 3 H, $\mathrm{C}H_2\mathrm{{=}CHCH_2}$), 5.25 (dq, $J = 17.3$, 1.7 Hz, 3 H, $\mathrm{C}H_2\mathrm{{=}CHCH_2}$), 5.82−5.95 (m, 3 H, $\mathrm{CH_2{=}C}H\mathrm{CH_2}$).

^{1}H NMR (300 MHz, $\mathbf{CDCl_3}$) Spectra of Perylene Diimide Derivatives (1 and 2). *N,N′-Bis[2-[3,5-bis[2-[2-(1-butoxy)ethoxy]ethoxy]phenyl]ethyl]perylene-3,4,9,10-tetracarboxyldiimide (PPEIEEB,* ***1b****):* δ 0.92 (t, $J = 7.4$ Hz, 12 H, $\mathrm{OCH_2CH_2CH_2C}H_3$), 1.37 (br sextet, $J = 7.4$ Hz, 8 H, $\mathrm{OCH_2CH_2C}H_2\mathrm{CH_3}$), 1.58 (br quintet, $J = 7.4$ Hz, 8 H, $\mathrm{OCH_2C}H_2\mathrm{CH_2CH_3}$), 2.98 (br t, $J = 8.1$ Hz, 4 H, $\mathrm{C}H_2\mathrm{CH_2N}$), 3.48 (t, $J = 6.6$ Hz, 8 H, $\mathrm{OC}H_2\mathrm{CH_2CH_2CH_3}$), 3.60−3.63 (m, 8 H, $\mathrm{OC}H_2$), 3.71−3.74 (m, 8 H, $\mathrm{OC}H_2$), 3.85 (br t, $J = 4.8$ Hz, 8 H, $\mathrm{OC}H_2$), 4.12 (br t, $J = 4.8$ Hz, 8 H, $\mathrm{OC}H_2$), 4.40 (br t, $J = 8.1$ Hz, 4 H, $\mathrm{CH_2C}H_2\mathrm{N}$), 6.40 (t, $J = 2.1$ Hz, 2 H, Ar-*H*), 6.57 (d, $J = 2.1$ Hz, 4 H, Ar-*H*),0.8.65 (d, $J = 8.1$ Hz, 4 H, Ar-*H*), 8.72 (d, $J = 8.1$ Hz, 4 H, Ar-*H*).

N,N′-Bis[2-[3,5-bis[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]phenyl]ethyl]perylene-3,4,9,10-tetracarboxyldiimide (PPEIEEEM, ***1c****):* δ 2.98 (br t, $J = 7.8$ Hz, 4 H, $\mathrm{C}H_2\mathrm{CH_2N}$), 3.39 (s, 12 H, $\mathrm{OC}H_3$), 3.55−3.58 (m, 8 H, $\mathrm{OC}H_2$), 3.66−3.77 (m, 24 H, $\mathrm{OC}H_2$), 3.85 (br t, $J = 4.8$ Hz, 8 H, $\mathrm{OC}H_2$), 4.12 (br t, $J = 4.7$ Hz, 8 H, $\mathrm{OC}H_2$), 4.41 (br t, $J = 8.1$ Hz, 4 H, $\mathrm{CH_2C}H_2\mathrm{N}$), 6.40 (t, $J = 2.1$ Hz, 2 H, Ar-*H*), 6.56 (d, $J = 2.1$ Hz, 4 H, Ar-*H*), 8.62 (d, $J = 8.1$ Hz, 4 H, Ar-*H*), 8.70 (d, $J = 8.1$ Hz, 4 H, Ar-*H*).

N,N′-Bis[2-[3,5-bis[2-(2-methoxyethoxy)ethoxy]phenyl]ethyl]-perylene-3,4,9,10-tetracarboxyldiimide (PPEIEEM, ***1d****):* δ 2.98 (br t, $J = 8.1$ Hz, 4 H, $\mathrm{C}H_2\mathrm{CH_2N}$), 3.40 (s, 12 H, $\mathrm{OC}H_3$), 3.57−3.60 (m, 8 H, $\mathrm{OC}H_2$), 3.71−3.74 (m, 8 H, $\mathrm{OC}H_2$), 3.85 (br t, $J = 4.8$ Hz, 8 H, $\mathrm{OC}H_2$), 4.13 (br t, $J = 4.8$ Hz, 8 H, $\mathrm{OC}H_2$), 4.41 (br t, $J = 8.3$ Hz, 4 H, $\mathrm{CH_2C}H_2\mathrm{N}$), 6.40 (t, $J = 2.1$ Hz, 2 H, Ar-*H*), 6.57 (d, $J = 2.1$ Hz, 4 H, Ar-*H*), 8.64 (d, $J = 7.8$ Hz, 4 H, Ar-*H*), 8.71 (d, $J = 8.1$ Hz, 4 H, Ar-*H*).

N,N′-Bis[3-[2-[2-(1-butoxy)ethoxy]ethoxy]propyl]perylene-3,4,9,-10-tetracarboxyldiimide (PPEEB, ***2b****):* δ 0.89 (t, $J = 7.7$ Hz, 6 H, $\mathrm{OCH_2CH_2CH_2C}H_3$), 1.32 (br sextet, $J = 7.4$ Hz, 4 H, $\mathrm{OCH_2CH_2C}H_2\mathrm{CH_3}$), 1.53 (br quintet, $J = 7.1$ Hz, 4 H, $\mathrm{OCH_2C}H_2\mathrm{CH_2CH_3}$), 2.08 (br quintet, $J = 6.7$ Hz, 4 H, $\mathrm{CH_2C}H_2\mathrm{CH_2N}$), 3.42 (t, $J = 6.8$ Hz, 4 H, $\mathrm{OC}H_2\mathrm{CH_2CH_2CH_3}$), 3.52−3.55 (m, 4 H, $\mathrm{OC}H_2$), 3.59−3.67 (m, 16 H, $\mathrm{OC}H_2$ and $\mathrm{C}H_2\mathrm{CH_2CH_2N}$), 4.31 (br t, $J = 7.1$ Hz, 4 H, $\mathrm{CH_2CH_2C}H_2\mathrm{N}$), 8.43 (d, $J = 8.4$ Hz, 4 H, Ar-*H*), 8.56 (d, $J = 8.1$ Hz, 4 H, Ar-*H*).

N,N′-Bis[3-[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]propyl]-perylene-3,4,9,10-tetracarboxyldiimide (PPEEEM, ***2c****):* δ 2.08 (br quintet, $J = 6.6$ Hz, 4 H, $\mathrm{CH_2C}H_2\mathrm{CH_2N}$), 3.36 (s, 6 H, $\mathrm{OCH_3}$), 3.51−3.54 (m, 4 H, $\mathrm{OC}H_2$), 3.61−3.66 (m, 24 H, $\mathrm{OC}H_2$), 4.32 (br t, $J = 7.1$ Hz, 4 H, $\mathrm{CH_2CH_2C}H_2\mathrm{N}$), 8.58 (d, $J = 8.4$ Hz, 4 H, Ar-*H*), 8.66 (d, $J = 8.1$ Hz, 4 H, Ar-*H*).

N,N′-Bis[3-[1,3-bis(2-methoxyethoxy)-2-propoxy]propyl]perylene-3,4,9,10-tetracarboxyldiimide (PPMEM, ***2d****):* δ 2.06 (br quintet, $J = 6.7$ Hz, 4 H, $\mathrm{CH_2C}H_2\mathrm{CH_2N}$), 3.36 (s, 12 H, $\mathrm{OC}H_3$), 3.50−3.69 (m, 26 H, $\mathrm{C}H_2\mathrm{C}H_2\mathrm{OC}H_2\mathrm{C}H$), 3.76 (t, $J = 6.2$ Hz, 4 H, $\mathrm{C}H_2\mathrm{CH_2CH_2N}$), 4.32 (br t, $J = 7.0$ Hz, 4 H, $\mathrm{CH_2CH_2C}H_2\mathrm{N}$), 8.61 (d, $J = 8.1$ Hz, 4 H, Ar-*H*), 8.68 (d, $J = 7.8$ Hz, 4 H, Ar-*H*).

N,N′-Bis[3-[1,3-bis[2-(2-methoxyethoxy)ethoxy]-2-propoxy]-propyl]perylene-3,4,9,10-tetracarboxyldiimide (PPMEEM, ***2e****):* δ 2.05 (br quintet, $J = 6.8$ Hz, 4 H, $\mathrm{CH_2C}H_2\mathrm{CH_2N}$), 3.37 (s, 12 H, $\mathrm{OC}H_3$), 3.52−3.65 (m, 42 H, $\mathrm{OC}H_2$ and $\mathrm{C}H\mathrm{O}$), 3.75 (t, $J = 6.3$ Hz, 4 H, $\mathrm{C}H_2\mathrm{CH_2CH_2N}$), 4.32 (br t, $J = 7.4$ Hz, 4 H, $\mathrm{CH_2CH_2C}H_2\mathrm{N}$), 8.62 (d, $J = 7.8$ Hz, 4 H, Ar-*H*), 8.69 (d, $J = 7.5$ Hz, 4 H, Ar-*H*).

N,N′-Bis[3-[2,2,2-tris(allyloxymethyl)ethoxy]propyl]perylene-3,4,9,10-tetracarboxyldiimide (PPOPAl, ***2f****):* δ 2.04 (br quintet, $J = 6.9$ Hz, 4 H, $\mathrm{CH_2C}H_2\mathrm{CH_2N}$), 3.44 (s, 12 H, $\mathrm{C}H_2\mathrm{O}$), 3.46 (s, 4 H, $\mathrm{C}H_2\mathrm{OCH_2CH_2CH_2N}$), 3.57 (t, $J = 6.3$ Hz, 4 H, $\mathrm{C}H_2\mathrm{CH_2CH_2N}$), 3.92 (br d, $J = 5.4$ Hz, 12 H, $\mathrm{CH_2{=}CHC}H_2$), 4.30 (br t, $J = 7.5$ Hz, 4 H, $\mathrm{CH_2CH_2C}H_2\mathrm{N}$), 5.11 (dq, $J = 10.8$, 1.5 Hz, 6 H, $\mathrm{C}H_2\mathrm{{=}CHCH_2}$), 5.23 (dq, $J = 17.3$, 2.0 Hz, 6 H, $\mathrm{C}H_2\mathrm{{=}CHCH_2}$), 5.80−5.93 (m, 6 H, $\mathrm{CH_2{=}C}H\mathrm{CH_2}$), 8.61 (d, $J = 8.1$ Hz, 4 H, Ar-*H*), 8.69 (d, $J = 7.8$ Hz, 4 H, Ar-*H*).

N,N′-Bis[2-[2,2,2-tris(allyloxymethyl)acetamido]ethyl]perylene-3,4,9,10-tetracarboxyldiimide (PENPAl, ***2g****):* δ 3.60 (s, 12 H, $\mathrm{OC}H_2$), 3.72 (br q, $J = 5.6$ Hz, 4 H, $\mathrm{C}H_2\mathrm{CH_2N}$), 3.87 (dt, $J = 5.5$, 1.6 Hz, 12 H, $\mathrm{CH_2{=}CHC}H_2$), 4.42 (br t, $J = 5.6$ Hz, 4 H, $\mathrm{CH_2C}H_2\mathrm{N}$), 5.01 (dq, $J = 10.4$, 1.6 Hz, 6 H, $\mathrm{C}H_2\mathrm{{=}CHCH_2}$), 5.13 (dq, $J = 17.3$, 1.8 Hz, 6 H, $\mathrm{C}H_2\mathrm{{=}CHCH_2}$), 5.66−5.79 (m, 6 H, $\mathrm{CH_2{=}C}H\mathrm{CH_2}$), 7.42 (t, $J = 5.6$, 2 H, $\mathrm{CON}H$), 8.54 (d, $J = 8.1$ Hz, 4 H, Ar-*H*), 8.63 (d, $J = 8.1$ Hz, 4 H, Ar-*H*).

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