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Practical synthesis of perylene-monoimide building blocks that possess features appropriate for use in porphyrin-based light-harvesting arrays

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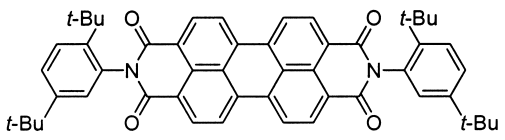
Abstract—Perylene-monoimide dyes with solubilizing aryloxy substituents at the perylene perimeter and a synthetic handle on the *N*-aryl group are valuable building blocks for incorporation as accessory pigments in porphyrin-based light-harvesting arrays. A family of such dyes has been prepared by reaction of 1,6,9-tris(4-*tert*-butylphenoxy)perylene-3,4-dicarboxylic anhydride with a set of 4-iodo/ethynyl anilines (with or without 2,6-diisopropyl substituents) in the presence of $Zn(OAc)_2{\cdot}2H_2O$ in imidazole/mesitylene at 130°C. The workup procedures throughout the synthesis have been streamlined for scale-up purposes, minimizing chromatography. Two bis(perylene)porphyrin building blocks were prepared in a rational manner and examined in Sonogashira and Glaser polymerizations. The two isopropyl groups on the *N*-aryl group and the three 4-*tert*-butylphenoxy groups at the perylene perimeter are essential for high solubility of the bis(perylene)porphyrins and corresponding oligomers in organic solvents.

1. Introduction

Perylene dyes have found widespread applications ranging from industrial pigments to components of molecular photonic devices.[1,2] In most cases, perylene-bis(imide) dyes (e.g. **1**) have been employed rather than perylene-monoimide dyes (e.g. **2**) (Chart 1). Both types of perylene-imide dyes have optical features that make them candidates for use as accessory pigments in conjunction with porphyrins. However, perylene-bis(imide) dyes easily undergo photo-induced reduction, an undesired process in light-harvesting arrays.[2–4] Perylene-monoimide dyes are more resistant toward reduction than perylene-bis(imide) dyes,[5–8] making the former quite attractive for use in light-harvesting applications.

The synthetic chemistry of perylene-monoimide dyes has developed rapidly over the past few years. Langhals developed a method for converting the commercially available perylene-dianhydride **3** into perylene-monoimide **2**,[9] which provides the starting point in most routes to substituted perylene-monoimide dyes. Müllen has developed methods for halogenation and substitution of perylene-monoimide dyes[10–12] and has incorporated perylene-monoimide dyes in dendrimeric architectures.[13] Wasielewski has developed a variety of perylene-monoimide dyes for use in molecular photonic switches.[14–18] For light-harvesting studies, we have prepared several perylene-monoimide–porphyrin dyads,[5–7] a linear array of one perylene-monoimide and two or four porphyrins,[19] constructs with multiple perylene-monoimides surrounding one porphyrin,[20] and rod-like oligomers comprised of a porphyrin-based backbone with two or four perylene-monoimide dyes per porphyrin.[21]



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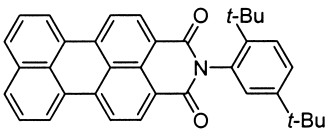

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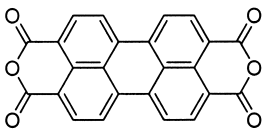

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Chart 1.

Keywords: perylene; perylene anhydride; perylene imide; imidation; porphyrin; light harvesting; accessory pigment.

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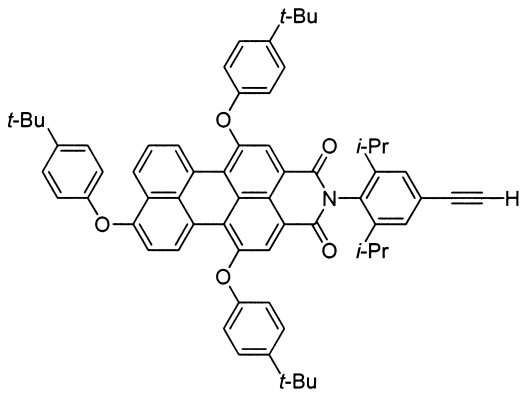
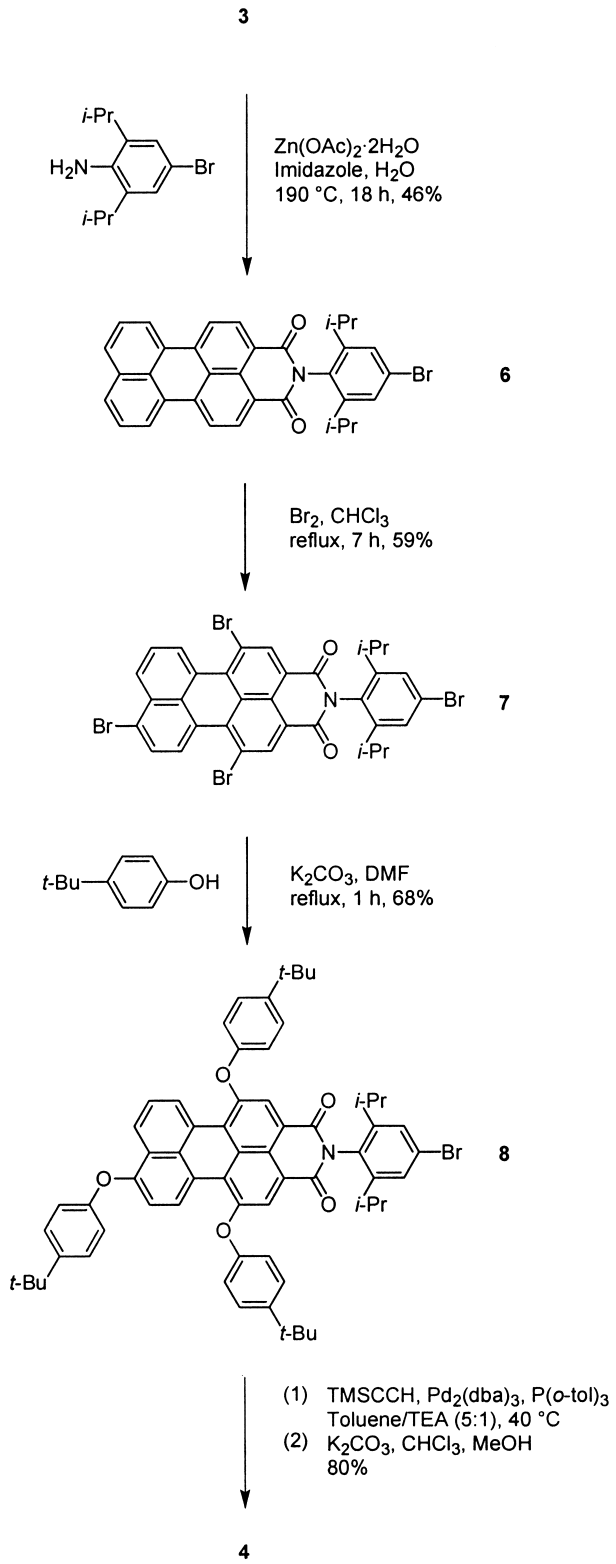


Chart 2.

A chief challenge in working with perylene-imide dyes is to overcome their intrinsically low solubility. A widespread approach with perylene-bis(imide) dyes has been to incorporate 2,5-di-*tert*-butyl[22,23] or 2,6-diisopropyl[10,24] substituents on aryl groups located at the *N*-imide positions. The absorption and emission characteristics of perylene-imide dyes are little affected by the presence of solubilizing substituents at the imide positions because of the nodes present at the imide nitrogen in both the HOMO and LUMO.[25] The same tactic of using alkylated *N*-aryl groups has been carried over to the perylene-monoimide dyes, but additional solubilizing features also have been sought by introducing aryloxy substituents at the perimeter of the perylene.[10,11] The aryloxy substituents cause a batho-chromic shift of the absorption and emission spectra and alter the electrochemical properties as well. After extensive studies of perylene–porphyrin dyads,[3–7] we found that the perylene-monoimide of choice for use with a porphyrin in a light-harvesting array has three aryloxy substituents (1, 6, and 9-positions) and a synthetic handle located on the *N*-aryl group (**4**, Chart 2). The use of three aryloxy groups affords a more soluble perylene dye than that substituted with one 9-aryloxy group (**5**).[20]

The synthetic strategy we employed to gain access to **4** is shown in Scheme 1.[7] The perylene-dianhydride **3** undergoes imidation and double decarboxylation upon reaction with the aniline bearing the desired synthetic handle, in this case 4-bromo-2,6-diisopropylaniline, forming perylene-mono-imide **6**. Bromination of **6** affords the tetrabromo derivative **7**, which undergoes regioselective aryloxylation to give the tris(aryloxy)perylene-monoimide **8** bearing the *p*-bromo substituent on the aryl group at the *N*-imide position. Direct coupling of **8** in dilute solution with ethynyl-porphyrins proceeded very poorly. However, ethynylation with (tri-methylsilyl)acetylene followed by deprotection provided access to a perylene-monoimide building block (**4**) that could be used in dilute-solution couplings.



Scheme 1.

There were two limitations in the synthetic approach outlined in Scheme 1. Strategically, the synthetic handle is introduced in the first step upon reaction with **3**. With this approach, the synthesis of other perylene-monoimides bearing different synthetic handles requires the entire synthesis to be performed. Practically, the yields in the synthesis were generally acceptable, but a number of

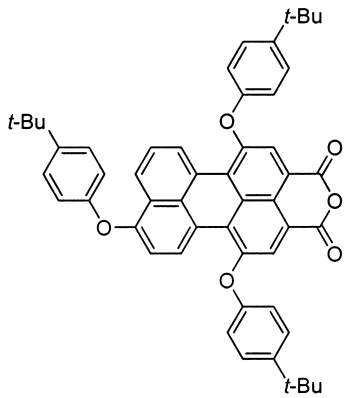


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Chart 3.

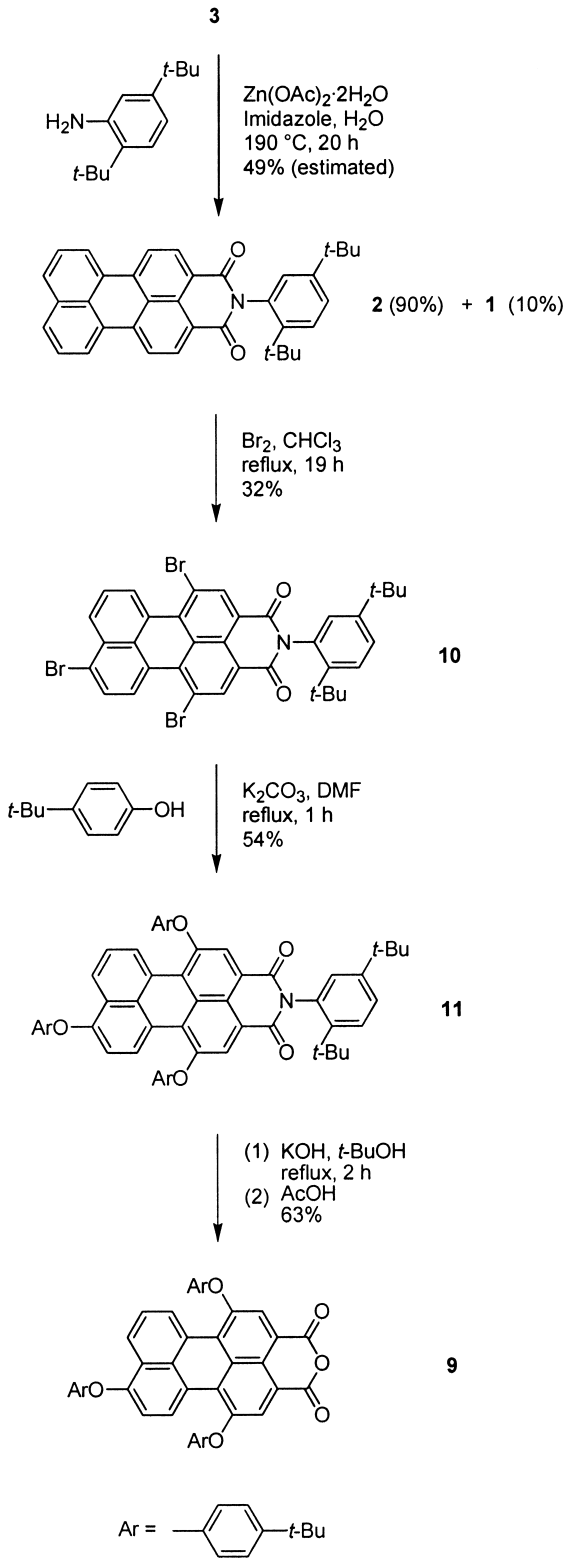
reactions employed extensive chromatography and multiple aqueous/organic extraction schemes for purification. Perylene-monoimide dyes typically can be readily precipitated but crystallize poorly. Thus, motivated by issues of strategy and practicality, we have worked to develop a new synthesis that provides access to a family of perylene-monoimide dyes without laborious chromatography.

Our results are presented in three parts. In Part 1, we describe the synthesis of a perylene-anhydride (**9**, Chart 3) that can be used in reactions with a variety of substituted anilines, thereby affording the corresponding perylene-monoimide dyes. The syntheses employ procedures in lieu of column chromatography that are rapid and amenable to scale up, including precipitation, trituration, filtration, vacuum filtration over short silica pads, and occasional use of aqueous/organic extractions. In Part 2, we employ several of the perylene-monoimide dyes in the synthesis of perylene–porphyrin building blocks. In Part 3, we investigate the preparation of several perylene–porphyrin arrays using the new perylene-monoimide dyes. One issue we have explored concerns the necessity of the solubilizing 2,6-diisopropyl groups on the aryl group at the *N*-imide position given the presence of aryloxy groups around the perimeter of the perylene, particularly when such dyes are incorporated in perylene–porphyrin arrays. Taken together, the approaches described herein should provide streamlined access to a variety of soluble perylene-monoimide dyes for use as building blocks in materials chemistry applications.

2. Results and discussion

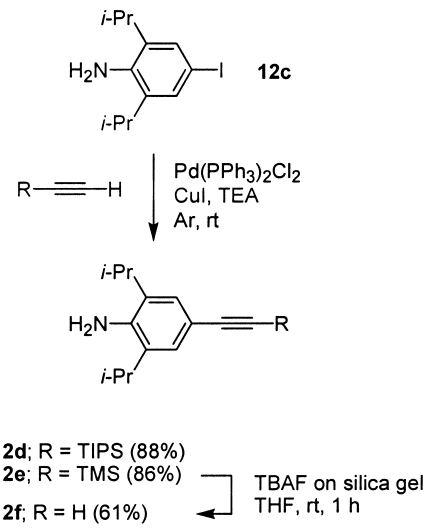
2.1. Synthesis of perylene-monoimide building blocks

Perylene-3,4:9,10-tetracarboxylic dianhydride (**3**) is available commercially in large quantities and has been used as the starting point in the synthesis of the monoimide **2**.[9] The latter has been used to prepare the tribromo monoimide **10**,[10,14,15] a versatile intermediate in the synthesis of perylene-monoimide dyes.[14–18] The synthesis of **2** employed extensive extraction followed by column chromatography, while the synthesis of **10** relied heavily on column chromatography. We followed the literature procedures for preparing **2** and **10** but modified the workup procedures.



Scheme 2.

Thus, treatment of **3** with 2,5-di-*tert*-butylaniline in the presence of $Zn(OAc)_2{\cdot}2H_2O$ in H_2O and imidazole at 190°C in an autoclave afforded a mixture of the perylene-bis(imide) **1** and the desired perylene-monoimide **2** (Scheme 2). The crude product was precipitated by addition of water, collected by filtration, and dried. A solution of the crude material was vacuum filtered through a pad of



Scheme 3.

silica, enabling removal of a small amount of perylene formed by exhaustive decarboxylation. The filtrate (CH_2Cl_2) contained the bis(imide) **1** and the monoimide **2**. Addition of methanol gave some selectivity in precipitation, affording **2** in ~90% purity (49% estimated yield) with the remaining ~10% consisting of **1**. While repeated fractional precipitation could afford a more pure product, the crude material was used directly in the bromination process because the bis(imide) **1** is more polar than **2** and can easily be removed in the workup of the tribrominated product **10**.

The crude sample of **2** was treated with excess Br_2 in $CHCl_3$ under reflux. TLC analysis showed two major products of nearly equal intensity with similar R_f values and a minor, more polar component. Vacuum filtration through a pad of silica yielded a filtrate containing compound **10** in ~90% purity. Evaporation of the filtrate, partial dissolution in CH_2Cl_2, and addition of hexanes yielded pure **10** as a solid in 32% yield that was collected by filtration.

Compound **10** was treated with 4-*tert*-butylphenol and K_2CO_3 in anhydrous DMF under reflux. (The reaction at lower temperature affords the 1,6-diaryloxy-9-bromo derivative.[10,14,15]) The addition of water followed by filtration afforded **11** and a major byproduct. Dissolution of the filtered material and vacuum filtration through a pad of silica gave the filtrate containing pure **11** in 54% yield.

The conversion of the imide to the anhydride proceeds through a base-mediated hydrolysis yielding the dicarboxylate intermediate, which subsequently undergoes acid-mediated dehydration.[9] Compound **11** was refluxed in the presence of KOH in 2-methyl-2-propanol followed by treatment with acetic acid. The addition of water yielded the anhydride as the dominant product and small amounts of a non-polar product (likely **11**) and a very polar byproduct (presumably the diacid). The crude material was dissolved and vacuum filtered through a pad of silica, yielding a filtrate containing the anhydride **9** and a trace amount of the polar byproduct. Evaporation to dryness, trituration with a small amount of methanol, and filtration afforded pure **9** in 63% yield. Removal of both impurities at this stage is essential for being able to purify the subsequent imidation product.

Perylene-anhydride **9** should be a versatile intermediate for preparing diverse perylene-monoimide dyes. Langhals has shown that perylene-3,4-dicarboxylic anhydrides undergo imidation with a variety of amines,[9] and Wasielewski has shown that related perylene-anhydrides undergo imidation with hydrazine[14,15] or a 4-(5-porphinyl)aniline.[17] We sought to condense **9** with several aniline derivatives, including 4-ethynylaniline (**12a**), 2,6-diisopropylaniline (**12b**), 4-iodo-2,6-diisopropylaniline (**12c**), and a 2,6-diisopropylaniline bearing an ethynyl group at the 4-position. For the latter, we examined 2,6-diisopropyl-4-[2-(triisopropylsilyl)ethynyl]-aniline (**12d**), 2,6-diisopropyl-4-[2-(trimethylsilyl)ethynyl]-aniline (**12e**), and 2,6-diisopropyl-4-ethynylaniline (**12f**). Anilines **12a** and **12b** are commercially available while **12c** is a known compound.[26] Sonogashira coupling of **12c** and (triisopropylsilyl)acetylene or (trimethylsilyl)acetylene afforded the corresponding aniline **12d** or **12e** in 88 or 86% yield, respectively (Scheme 3). Deprotection of **12e** with tetrabutylammonium fluoride (TBAF) on silica gel in THF at room temperature furnished **12f** in 61% yield. All aniline derivatives were purified by vacuum filtration through a pad of silica, affording analytically pure compounds.

The methods for imidation of perylene-anhydrides include reaction in the presence of zinc acetate in solvents such as molten imidazole,[9] pyridine,[23] or quinoline[23] at reflux. Similar imidations have been performed in DMF alone.[15] The reaction of perylene-anhydride **9** with 3 equiv. of 4-ethynylaniline (**12a**) was performed in the presence of $Zn(OAc)_2{\cdot}2H_2O$ in anhydrous DMF for 17 h (entry 1 in Table 1; Scheme 4). The addition of water yielded a precipitate consisting of the desired ethynyl-perylene (**13a**) as the dominant product, a small amount of perylene starting material, an unknown byproduct, and **12a**. TLC analysis showed the first three components to have similar polarities. The precipitate was washed with aqueous methanol to remove unreacted **12a**. The precipitate was dissolved and vacuum filtered through a pad of silica, affording a filtrate containing relatively pure ethynyl-perylene. The filtrate was evaporated and triturated with methanol to afford **13a** in 50% yield. Anhydride **9** was also treated with 3 equiv. of 4-ethynylaniline (**12a**) in the presence of $Zn(OAc)_2{\cdot}2H_2O$ in molten imidazole and mesitylene, affording **13a** in 64% yield (entry 2). The use of molten imidazole for the imidation of perylene-anhydride **9** gave higher yield and a shorter reaction time compared with the reaction in DMF.

The reaction of perylene-anhydride **9** with **12a** affords the ethynyl perylene-monoimide dye lacking isopropyl groups. The reaction of **9** with 2,6-diisopropyl-substituted anilines is expected to be more demanding owing to the steric hindrance of the amine. We employed the imidation of **9** with 2,6-diisopropylaniline (**12b**) affording perylene-monoimide **13b** as a benchmark for developing suitable reaction conditions for sterically hindered amines. The reaction in the presence of $Zn(OAc)_2{\cdot}2H_2O$ in DMF, pyridine, quinoline, or ethylene glycol resulted in recovery of the starting material. By the use of molten imidazole with mesitylene as a fluid cosolvent, the difficulties in the imidation with the

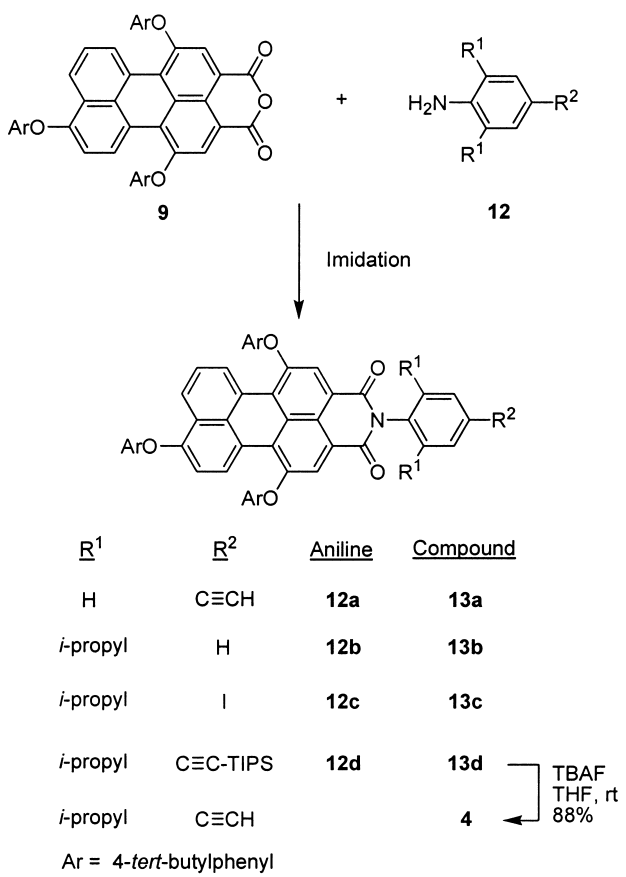
Table 1. Imidation of **9** with aniline derivatives

Entry	Product	Aniline (equiv.)	Solvent	Time (h)	Yield (%)
1[a]	**13a**	**12a** (3)	DMF	17	50
2	**13a**	**12a** (3)	Imidazole/mesitylene	2	64
3	**13b**	**12b** (3)	Imidazole/mesitylene	20	35
4	**13b**	**12b** (20)	Imidazole/mesitylene	24	40
5	**13c**	**12c** (3)	Imidazole/mesitylene	23	30
6	**4**	**12f** (3)	Imidazole/mesitylene	24	–[b]
7[a]	**13d**	**12d** (20)	Imidazole/mesitylene	36	48

Imidation was carried out at 130°C in the presence of $Zn(OAc)_2{\cdot}2H_2O$.
[a] Preparative scale.
[b] Starting material and/or product decomposed.

sterically hindered aniline were partly overcome, affording a 35% yield of **13b** (entry 3). An increase in the amount of 2,6-diisopropylaniline (~20 equiv.) gave a yield of 40% (entry 4). The synthesis of **13b** was done at a small scale with chromatographic workup.

The reaction conditions found to be best [$Zn(OAc)_2{\cdot}2H_2O$ in imidazole/mesitylene at 130°C] in preparing **13b** were applied to prepare other perylene-monoimides bearing different *N*-aryl units. In this manner, perylene-monoimide **13c** was prepared in 30% yield (entry 5), also at a small scale with chromatographic workup. The synthesis of perylene-monoimide **4**, which has a free ethyne on the aniline component, could not be obtained via imidation with anhydride **9**, probably due to decomposition during the long reaction (entry 6). However, the TIPS-protected ethynylaniline **12d** reacted with anhydride **9** affording compound **13d** as the dominant product accompanied by unreacted **12d** and polar byproducts. The reaction mixture was extracted with CH_2Cl_2, washed with water to remove salt and imidazole, and the resulting residue was purified by vacuum filtration through a pad of silica followed by trituration with methanol, affording **13d** in 48% yield (entry 7). Treatment of **13d** with TBAF in THF gave **4** accompanied by a small amount of polar byproducts. Vacuum filtration of the crude mixture through a pad of silica followed by trituration with methanol afforded **4** in 88% yield (Scheme 4). In summary, the synthesis of pure perylene-monoimide dyes **13a–d** was achieved by imidation of perylene-anhydride **9**. For preparative scale syntheses, the use of vacuum filtration, precipitation, and trituration proved to be a viable substitute for chromatography and extraction procedures.

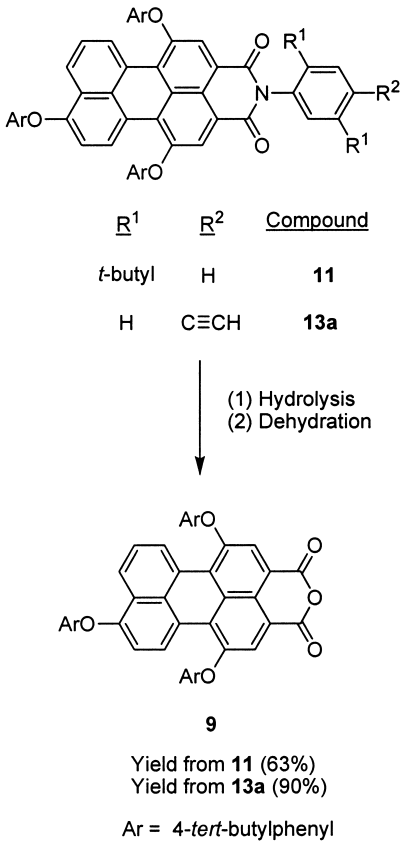


Scheme 4.

We also found that perylene-monoimide **13a** could be used as a starting material for preparing perylene-anhydride **9** (Scheme 5). The conditions employed were similar to those in the synthesis of **9** from **11** (Scheme 2). Perylene **13a** was refluxed with KOH in 2-methyl-2-propanol for 2 h. After treatment with acetic acid followed by addition of water, anhydride **9** was obtained as a pre-cipitate which was purified by vacuum filtration through a pad of silica and trituration with methanol. These results show that the perylene-monoimide bearing an unhindered *N*-imide aryl group can be converted to the perylene-anhydride in excellent yield.

2.2. Synthesis of perylene–porphyrin building blocks lacking isopropyl groups

We previously prepared bis(perylene)porphyrin building blocks wherein each perylene-monoimide dye was substituted with two isopropyl substituents on the *N*-imide aryl group, as well as with three aryloxy groups at the perimeter of the perylene (**14**, **15**, Chart 4).[21] Building block **14** is an ABCD-porphyrin that bears one iodo group and one ethyne group in a *trans* architecture for Sonogashira coupling, while **15** is a *trans*-AB_2C-porphyrin that bears two ethyne groups for Glaser coupling. The Y-shaped architecture of **14** and **15** was designed to preclude cofacial aggregation of the porphyrin macrocycles while still maintaining efficient energy transfer from the perylene to the porphyrin. Indeed, **14** and **15** exhibit efficient energy transfer from perylene to porphyrin, are highly soluble in organic solvents, and were converted into rod-like oligomers that also exhibited high solubility.[21]



Scheme 5.

Early in the development of perylene-imide dyes, it became apparent that bulky *N*-imide groups were essential for achieving workable solubility in organic solvents.[22,23,27] Aryloxy substituents were subsequently introduced at the perimeter of the perylene thereby further increasing the solubility.[10,11] Given the Y-shaped architecture of the bis(perylene)porphyrins, we wondered whether the alkyl groups on the *N*-imide aryl group, or fewer 4-*tert*-butylphenoxy groups, were in fact essential for solubility of the bis(perylene)porphyrins. The availability of the new perylene-monoimide dyes provided an opportunity to address this question, prompting us to prepare the perylene–porphyrins **16** and **17** (Chart 4), which are analogs of **14** and **15**.

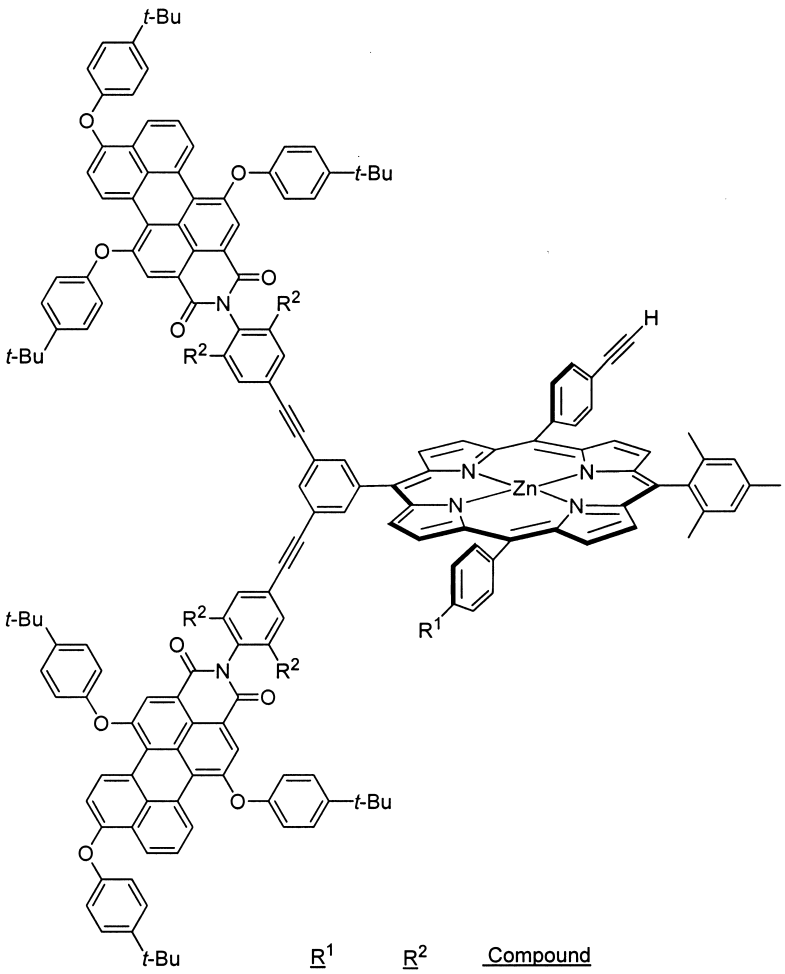
The synthesis of porphyrins bearing distinct patterns of *meso*-substituents can be achieved in a rational manner by reaction of a dipyrromethane and a dipyrromethane–dicarbinol.[28] The synthesis of a dipyrromethane requires access to the corresponding precursor aldehyde.[29] A 3,5-bis-(perylene)benzaldehyde and the corresponding bis(perylene)phenyldipyrromethane served as valuable intermediates in the synthesis of perylene–porphyrin building blocks **14** and **15**.[21] This same approach was employed in the synthesis of **16** and **17**.

We found previously that the Sonogashira coupling to make the bis(perylene)benzaldehyde **20** was very sensitive to the type of substituent on the *N*-aryl moiety. For example, the synthesis of **20** via coupling of ethynyl-perylene **4** with commercially available 3,5-dibromobenzaldehyde (**18**, 83% yield, entry 1 in Table 2, Scheme 6) was superior to the coupling of bromo-perylene (**8**) and 3,5-diethynylbenzaldehyde (**19**,[30] 8.9% yield, entry 2). The disparity in coupling yield is easily attributed to the less active bromine at the 4-position of the perylene *N*-imide substituted aryl moiety compared with the bromines at the 3 and 5-positions of benzaldehyde.[20] The availability of iodo-perylene **13c** presented an opportunity to perform the coupling with a more active halogen on the perylene-monoimide dye. Thus, Sonogashira coupling of **13c** with **19** afforded **20** in 42% yield (entry 3). This result was somewhat improved compared with the combination of bromo-perylene and **19** (8.9% yield); however, the use of the ethynyl-perylene and **18** provided the best yields in the preparation of bis(perylene)benzaldehyde **20**.

Sonogashira coupling of ethynyl-perylene **5**[7] and **18** afforded perylene-aldehyde **21** in 35% yield (entry 4 in Table 2, Scheme 6). The coupling reaction was performed in toluene/triethylamine (10:1) at 60°C with the perylene at a concentration of 14 mM. Unfortunately, compound **21** exhibited poor solubility (<1 mg/mL in $CDCl_3$) and attempts to prepare the corresponding tetrakis(perylene)-porphyrin by condensation of **21** with 5-mesityldipyrromethane[29] proved unsuccessful. No further studies were performed with **21**. A bis(perylene)benzaldehyde lacking isopropyl groups (**22**) was prepared by Sonogashira coupling of **13a** (2.4 equiv.) and **18** in the presence of CuI in 69% yield (entry 5).[20] The reaction mixture was initially heterogeneous, became homogeneous upon increasing the temperature, and afforded aldehyde **22** as a precipitate, indicating limited solubility. In summary, the solubility of the bis(perylene)benzaldehydes increases in the following series: **21** (isopropyl groups but only one aryloxy substituent)<**22** (no isopropyl groups but three aryloxy substituents)<**20** (isopropyl groups and three aryloxy substituents).

The synthesis of dipyrromethanes is readily achieved at room temperature by the reaction of an aldehyde in excess neat pyrrole (25:1 molar ratio of pyrrole–aldehyde) upon addition of a catalytic amount of TFA.[29] Very recently, we found that the dipyrromethane synthesis with **20** performed with inclusion of a small amount of CH_2Cl_2 (3:1 v:v pyrrole/CH_2Cl_2) and a much larger molar ratio of pyrrole–aldehyde (400:1) affords a significant enhancement in the yield.[21] The CH_2Cl_2 in this case was essential to solubilize the bis(perylene)benzaldehyde **20**, which was insoluble in neat pyrrole, but apparently the slight dilution achieved in doing so as well as the increased pyrrole–aldehyde ratio is quite beneficial to the synthesis. We employed the same modified method here. Thus, the reaction of aldehyde **22** and excess pyrrole (400-fold) in CH_2Cl_2 (25% by volume) using TFA as a catalyst gave bis(perylene)dipyrromethane **23** in 96% yield (Scheme 7). Dipyrromethane **23** served as a key compound for preparing the perylene–porphyrin monomers required in Sonogashira and Glaser polymerizations.

The dipyrromethane+dipyrromethane–dicarbinol condensation leading to *meso*-substituted porphyrins has typically been carried out at room temperature in CH_3CN using TFA catalysis.[28] The choice of catalytic conditions is essential to avoid acidolysis of the dipyrromethane followed by undesired recombination of fragments, leading to a mixture



R^1	R^2	Compound
I	*i*-Pr	**14** (ref 21)
C≡CH	*i*-Pr	**15** (ref 21)
I	H	**16**
C≡CH	H	**17**

Chart 4.

of porphyrins (i.e. scrambling). Recently we found that the use of selected mild, Lewis acids in CH_2Cl_2 at room temperature affords the porphyrin without detectable scrambling and often with higher yields than that obtained with TFA in CH_3CN.[31] We employed the new acid catalysis conditions in this work. Thus, the condensation of **23** with **24**-diol, which is obtained from reduction of the diacyldipyrromethane **24** using $NaBH_4$ in THF/methanol (10:1), was performed in the presence of $Yb(OTf)_3$ in CH_2Cl_2 at room temperature. Subsequent oxidation with DDQ and metalation with $Zn(OAc)_2{\cdot}2H_2O$ at room temperature afforded porphyrin **16** in 10% yield. In the same manner,

Table 2. Sonogashira couplling of ethynyl/halide–perylene and dibromo/diethynyl-benzaldehyde

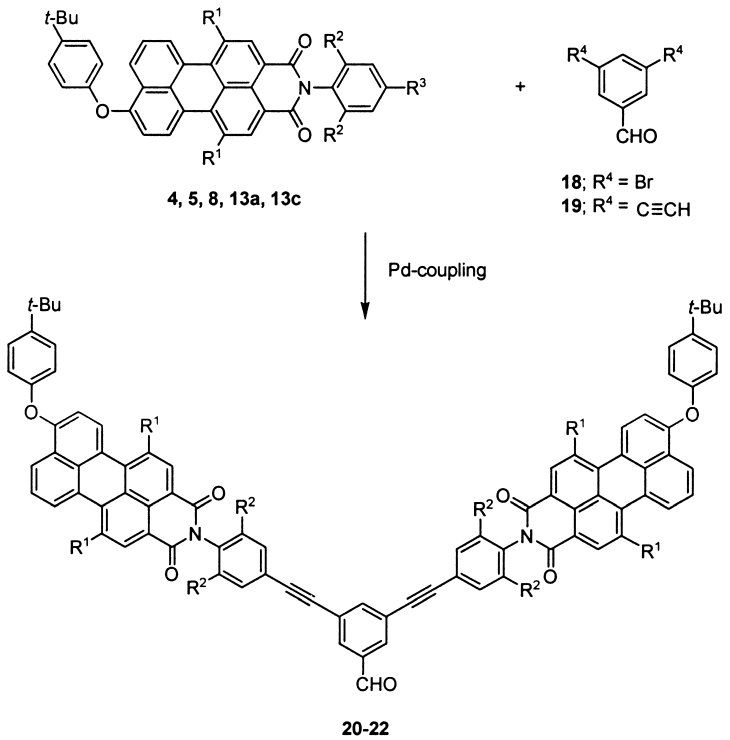
Entry	R^1	R^2	R^3	R^4	Perylene	Aldehyde	Compound (perylene+aldehyde)	Yield (%)
1	4-*t*-Butylphenoxy	*i*-Pr	C≡CH	Br	**4**	**18**	**20**	83
2	4-*t*-Butylphenoxy	*i*-Pr	Br	C≡CH	**8**	**19**	**20**	8.9[a]
3	4-*t*-Butylphenoxy	*i*-Pr	I	C≡CH	**13c**	**19**	**20**	42[b]
4	H	*i*-Pr	C≡CH	Br	**5**	**18**	**21**	35[c]
5	4-*t*-Butylphenoxy	H	C≡CH	Br	**13a**	**18**	**22**	69

The Pd-coupling reaction was carried out under the following conditions unless otherwise noted: [perylene]=12 mM, [aldehyde]=5.0 mM, catalysts=$Pd_2(dba)_3$, PPh_3, and CuI, solvent=toluene/TEA (5:1), temperature=50°C (Ref. 20).

[a] [Perylene]=10 mM, [aldehyde]=5.0 mM, $Pd_2(dba)_3$ and P(*o*-tol)$_3$, 60°C (Ref. 20).

[b] $Pd_2(dba)_3$, P(*o*-tol)$_3$, 40°C.

[c] [Perylene]=14 mM, [aldehyde]=6.0 mM, $Pd_2(dba)_3$, P(*o*-tol)$_3$, toluene/TEA (10:1), 60°C.



Scheme 6.

porphyrin **17** was prepared by the condensation of dipyrromethane **23** and **25**-diol in 31% yield. In both cases, no scrambling was detected upon mass spectral analysis of the crude reaction samples. However, both perylene–porphyrins **16** and **17** have lower solubility than their analogs bearing isopropyl groups (**14**, **15**).

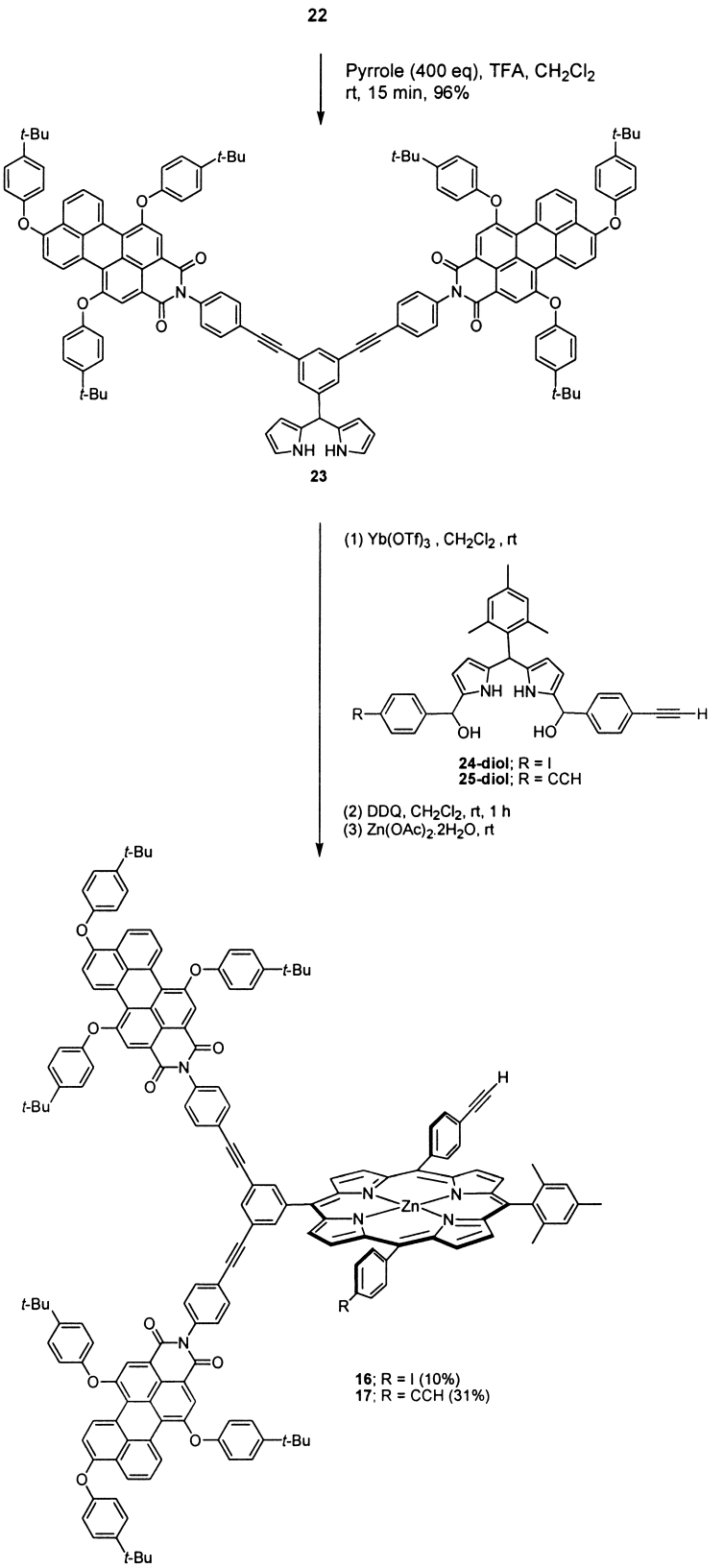
2.3. Oligomeric bis(perylene)porphyrin arrays

We previously subjected perylene–porphyrin building blocks to Sonogashira and Glaser polymerizations, affording diphenylethyne- or diphenylbutadiyne-linked oligomers, respectively.[21] The oligomers were of considerable size and exhibited adequate solubility in common organic solvents (THF, $CHCl_3$, CH_2Cl_2, toluene) for routine processing and characterization. The same routes were employed for preparing oligomers of bis(perylene)porphyrin monomers lacking isopropyl groups.

A Sonogashira polymerization of **16** was performed under argon at room temperature in the presence of $Pd_2(dba)_3$ and $AsPh_3$ in toluene/triethylamine. After 22 h, the reaction mixture became heterogeneous and analytical size exclusion chromatography (SEC) of a dissolved sample revealed the formation of oligomers up to the pentamer stage. The amount of these oligomers increased slightly after 40 h. Analytical SEC of the suspended solid in the reaction mixture (obtained by dissolving the solid in THF with sonication) showed the presence of short oligomers. The low solubility of these short oligomers likely impeded the formation of longer oligomers. Therefore, we next examined the Glaser polymerization, which typically is more rapid and gives longer oligomers compared with those given by Sonogashira coupling.[21]

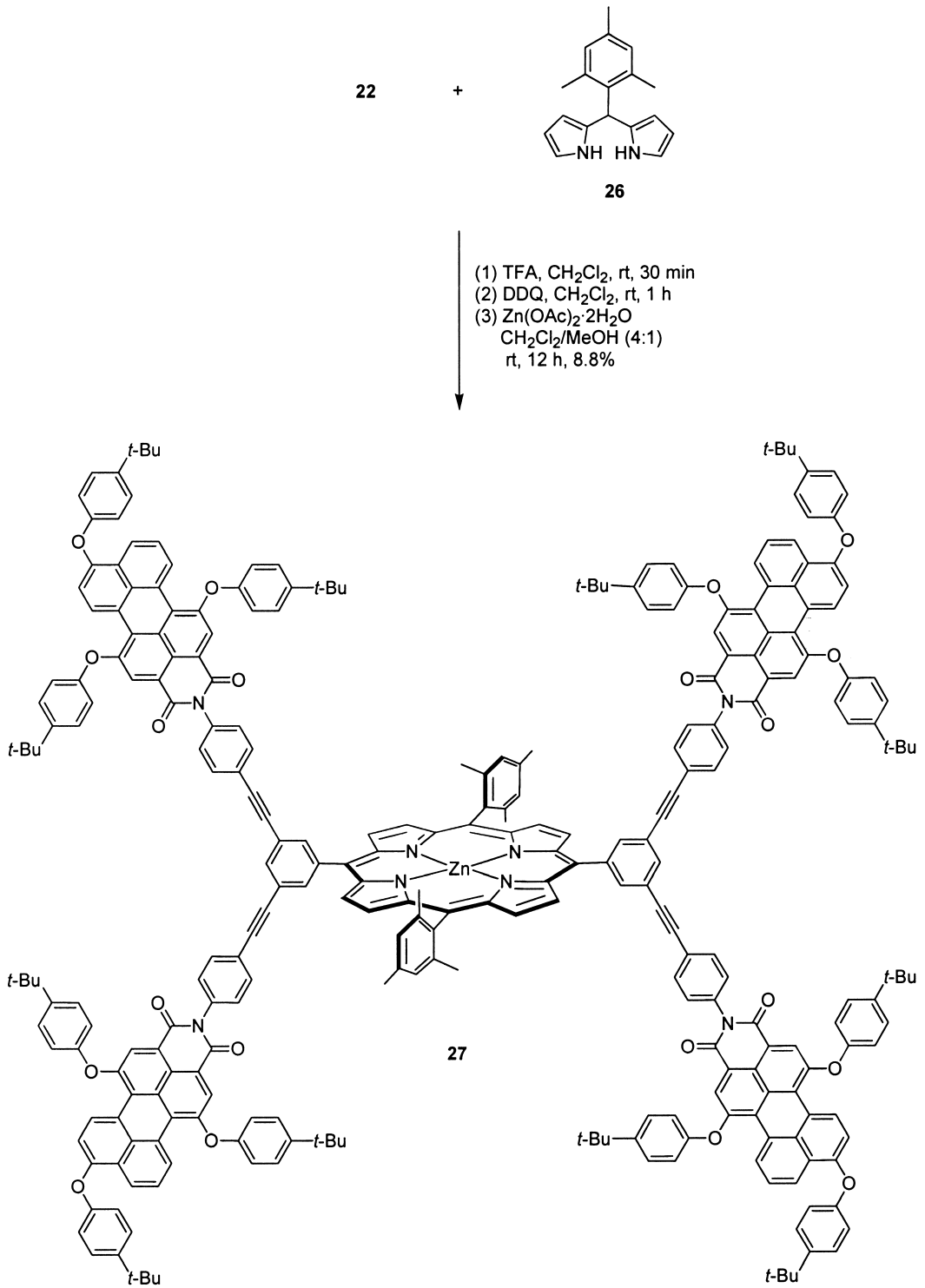
The Glaser reaction of **17** was carried out with $Pd(PPh_3)_2Cl_2$ and CuI in toluene/diisopropylethylamine at room temperature in the presence of air. A slight amount of precipitation appeared to form. After 3 h, analytical SEC of a dissolved reaction sample showed a distribution of the starting monomer and oligomers up to the octamer stage. The monomer, dimer, reagents and small byproducts were removed by preparative SEC. The resulting crude product was further purified by triturating with methanol and hexanes. The resulting magenta powder could be dissolved in THF, was partially soluble in $CHCl_3$ and CH_2Cl_2, but was only slightly soluble in toluene. While the diphenylbutadiyne-linked oligomers (Glaser reaction) appeared to be more soluble than the diphenylethyne-linked oligomers (Sonogashira reaction), further characterization of the oligomers derived from bis(perylene)porphyrins **16** and **17** was not attempted.

To investigate the optical properties of a tetrakis(perylene)porphyrin wherein each perylene lacks isopropyl substituents, we prepared porphyrin **27** (Scheme 8). Bis(perylene)benzaldehyde **22** and 5-mesityldipyrromethane (**26**)[29] were condensed at room temperature in CH_2Cl_2 with TFA catalysis, conditions that are known to afford reaction without scrambling.[32] Oxidation with DDQ and metalation with $Zn(OAc)_2{\cdot}2H_2O$ at room temperature afforded porphyrin **27** in 8.8% yield. Compound **27** is soluble in $CHCl_3$ but could hardly be dissolved in CH_2Cl_2 or toluene. Indeed, a sample was marginally soluble in toluene at the μM concentration, requiring warming and sonication to collect a visible absorption spectrum. In contrast, the analogous tetrakis(perylene)porphyrin wherein each perylene bears two isopropyl groups on the *N*-imide aryl group,[20] was highly soluble in $CHCl_3$, CH_2Cl_2 or toluene.



Scheme 7.

The absorption spectrum of **27** displayed the characteristic bands of the zinc porphyrin and the perylene-monoimide. The Soret band of the zinc porphyrin was sharp (fwhm=13 nm) and resembled that of a porphyrin lacking perylene substituents, indicating that any electronic interactions between the porphyrin and perylenes are rather weak. However, excitation at 540 nm, where the perylene-monoimide absorbs preferentially, resulted in emission predominantly from the zinc porphyrin. The spectral data, which are nearly identical to those of the



Scheme 8.

tetrakis(perylene)porphyrin analog bearing isopropyl groups flanking the *N*-imide position,[20] are indicative of efficient energy transfer from the perylene-monomide units to the porphyrin. Thus, the perylene-monoimide dyes in **27** provide absorption in the spectral region where the porphyrin absorbs weakly, do not alter the energy levels of the porphyrin as shown by the absorption spectrum, and transfer energy to the porphyrin with good efficiency, all of which are features of viable accessory pigments.

3. Conclusions

The synthesis of perylene-anhydride **9** enables the preparation of a family of perylene-monoimide dyes that differ only in the type of synthetic handle and solubilizing groups on the *N*-imide unit. This synthetic strategy has been implemented to minimize use of chromatography, relying instead on selective precipitation, trituration, filtration, and filtration over short pads of silica. Perylene-monoimide dyes were prepared that either incorporate or lack two isopropyl

groups at the 2,6-positions flanking the *N*-imide substituent on the aryl unit. The best method for preparing the dyes employs imidation of perylene-anhydride **9** with an aniline derivative in imidazole/mesitylene containing $Zn(OAc)_2{\cdot}2H_2O$ at 130°C. Two bis(perylene)porphyrin building blocks were prepared for Sonogashira and Glaser oligomerizations; one tetrakis(perylene)porphyrin array was prepared for fundamental spectroscopic studies. In each case, the perylene-monoimide dyes lacked isopropyl groups flanking the *N*-imide substituent. Each of the perylene–porphyrin monomers was sufficiently soluble for spectroscopic characterization and routine handling, though each array was less soluble than the analog in which the isopropyl groups were present. The solubility differences were exacerbated upon formation of diphenylethyne or diphenylbutadiyne-linked oligomers. The monomers lacking the isopropyl groups afforded oligomers that were shorter, owing to precipitation during the course of polymerization, than the oligomers derived from monomers in which the isopropyl groups were present. On the other hand, the synthesis of a bis(perylene)benzaldehyde (**21**) bearing the two flanking isopropyl groups but incorporating only one aryloxy substituent gave very poor solubility compared with that containing three aryloxy groups (**20**). Thus, adequate solubility of perylene–porphyrin arrays and oligomers requires the presence of two types of solubilizing features: three aryloxy groups at the perylene perimeter and two isopropyl groups flanking the *N*-imide moiety.

4. Experimental

4.1. General

^1H NMR spectra (300 or 400 MHz) and ^{13}C (75 MHz) were recorded in $CDCl_3$. Mass spectra of porphyrins and perylene–porphyrin compounds were obtained by high-resolution fast atom bombardment (FAB-MS) and by matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS). Absorption and emission spectra were collected in toluene at room temperature. Melting points are uncorrected. An autoclave (Roth Hochdruck-Laborautoklav Modell IV, Carl Roth GmbH & Co. KG, Karlsruhe, Germany) equipped with a voltage transformer (Simran, SM-1000DE) was used. Centrifugation was performed using a Dynac II tabletop centrifuge (4000 rpm). Sonication was performed using a Fisher FS14 tabletop sonication bath. Silica gel (Baker 40 μm average particle size) was used for vacuum filtration and column chromatography. Preparative SEC was performed using Biorad Bio-Beads SX-1 (200–400 mesh). Analytical SEC was performed using an HP 1100 Series Liquid Chromatograph (column size=a 10^4 Å column and a 10^3 Å column in series; flow rate=0.800 mL/min; solvent=THF; quantitation at 420 and 510 nm; reference at 670 nm; oven temperature 25°C).[33] All Sonogashira coupling reactions were performed using a Schlenk line. All Glaser coupling reactions were performed in air using $Pd(PPh_3)_2Cl_2$ and CuI. Palladium insertion and transmetalation of porphyrins have not been observed under these conditions.[34] Toluene and triethylamine were freshly distilled from CaH_2 and sparged of oxygen prior to use. All solvents and reagents were purchased from Aldrich and Fisher and used as received. Chloroform contained 0.8% ethanol as a stabilizer.

4.2. Non-commercial compounds

Compounds **12c**[26] and **19**;[30] diacyldipyrromethanes **24**[21] and **25**;[35] and 5-mesityldipyrromethane (**26**)[29] were prepared as described in the literature.

4.3. New synthetic compounds and procedures

4.3.1. *N*-(2,5-Di-*tert*-butylphenyl)perylene-3,4-dicarboximide (2). Following the procedure of Langhals,[9] samples of **3** (33.0 g, 84.2 mmol), 2,5-di-*tert*-butylaniline (9.47 g, 46.0 mmol), $Zn(OAc)_2{\cdot}2H_2O$ (3.97 g, 18.1 mmol), imidazole (169 g), and H_2O (72 mL) were placed in an autoclave equipped with a manometer. The mixture was stirred at 190°C. After 20 h, the manometer showed 15 bar and the reaction mixture was cooled to room temperature. Water (300 mL) was added to the reaction mixture. The resulting mixture was vacuum filtered over a single fritted glass filter. The filtered solid obtained was washed with 2N aqueous HCl/methanol [500 mL, (1:1)] then H_2O/methanol [300 mL, (1:1)] and dried in an oven at 130°C. TLC analysis (silica, CH_2Cl_2) showed the presence of the title compound (R_f=0.52, red) and **1** (R_f=0.21, orange). The crude solid was suspended in CH_2Cl_2 (300 mL) and vacuum filtered through a fritted glass filter, then washed with CH_2Cl_2 (500 mL) leaving insoluble byproducts on the filter. The filtrate was concentrated to a volume of ~300 mL and passed through a pad of silica (6.0×6.0 cm, swelled with CH_2Cl_2) in a fritted glass filter with CH_2Cl_2 (500 mL). A less polar, slightly yellow byproduct (perylene itself) eluted first and was not collected. Subsequent elution with CH_2Cl_2 (800 mL) afforded the title compound. The filtrate was concentrated to a volume of ~200 mL. Then methanol (200 mL) was added. A red solid precipitated upon standing at 0°C and was collected by filtration (12.7 g). The purity of the title compound obtained was estimated to be 90% [**1** accounts for the remaining 10%] by ^1H NMR spectroscopy. The yield is estimated to be 49% assuming the purity to be 90%. This material was used without further purification in the next step.

4.3.2. 1,6,9-Tribromo-*N*-(2,5-di-*tert*-butylphenyl)perylene-3,4-dicarboximide (10). Following the approach outlined by Müllen[10] and the procedure described in detail by Wasielewski,[14] a mixture containing crude **2** (13.3 g, assuming 26.1 mmol) and Br_2 (21.0 mL, 410 mmol) in $CHCl_3$ (400 mL) was refluxed for 19 h. The reaction mixture was concentrated to dryness. TLC analysis (silica, CH_2Cl_2) showed the presence of the title compound (R_f=0.83, red), a major byproduct (R_f=0.73, orange), and residual **1** (R_f=0.20, orange). The crude solid was suspended in toluene/hexanes [400 mL (1:1)] and vacuum filtered through a pad of silica [6.0×6.0 cm, swelled with toluene/hexanes (1:1)] in a fritted glass filter. Elution with toluene/hexanes [1.0 L (1:1)] removed a small amount of a yellow material; then elution with toluene/hexanes [3.0 L (1:1)] afforded the title compound in ~90% purity. Most of the impurities (the major byproduct and **1**) remained at the top of the silica pad. The eluant containing the title compound (~90% purity with an unknown compound

constituting the remaining ~10%) was concentrated to dryness. Addition of CH_2Cl_2 (100 mL) yielded a slurry, to which hexanes (200 mL) was added. The resulting red solid was collected by filtration (6.22 g, 32%). Characterization data were identical to those reported previously.[14]

4.3.3. 1,6,9-Tris(4-*tert*-butylphenoxy)-*N*-(2,5-di-*tert*-butylphenyl)perylene-3,4-dicarboximide (11). Following a procedure described for diaryloxylation[14] but at higher temperature and with excess 4-*tert*-butylphenol to achieve triaryloxylation, a mixture of **10** (9.90 g, 13.3 mmol), 4-*tert*-butylphenol (24.0 g, 160 mmol), and K_2CO_3 (26.5 g, 192 mmol) in anhydrous DMF (500 mL) was refluxed for 1 h. The reaction mixture was cooled to room temperature. TLC analysis [silica, CH_2Cl_2/hexanes (1:2)] showed the presence of the title compound (R_f=0.37, magenta) and a major byproduct (R_f=0.23, purple). Water (500 mL) was added to the reaction mixture. The resulting solid was collected by vacuum filtration in a fritted glass filter, washed with H_2O/methanol [500 mL (1:1)] while on the filter, and then dried in an oven at 130°C. The crude solid consisted of the title compound and a major byproduct. The crude solid was dissolved in CH_2Cl_2/hexanes [400 mL (1:4)] and vacuum filtered through a pad of silica [9.5×6.0 cm, swelled with CH_2Cl_2/hexanes (1:4)] on a fritted glass filter using CH_2Cl_2/hexanes [6.0 L (1:4)]. The byproduct remained on the silica pad. The filtrate was concentrated to give a magenta solid (6.90 g, 54%): mp 203–205°C; ^{1}H NMR δ 1.25 (s, 9H), 1.28 (s, 9H), 1.31 (s, 9H), 1.335 (s, 9H), 1.344 (s, 9H), 6.89–6.93 (m, 2H), 7.02 (d, J=8.8 Hz, 2H), 7.08 (d, J=8.8 Hz, 2H), 7.09 (d, J=8.8 Hz, 2H), 7.37 (d, J=8.8 Hz, 2H), 7.40–7.44 (m, 5H), 7.52–7.55 (m, 1H), 7.62–7.67 (m, 1H), 8.28 (s, 1H), 8.31 (s, 1H), 8.48 (d, J=8.1 Hz, 1H), 9.26 (d, J=8.8 Hz, 1H), 9.46 (d, J=8.1 Hz, 1H); ^{13}C NMR δ 31.4, 31.7, 32.0, 34.4, 34.6, 35.7, 111.9, 118.6, 118.8, 119.9, 120.9, 121.9, 122.5, 123.3, 124.4, 124.7, 126.1, 126.3, 126.5, 126.6, 126.8, 127.1, 127.3, 127.5, 127.7, 127.8, 128.0, 128.9, 129.9, 130.0, 130.9, 131.7, 132.9, 143.9, 147.2, 147.3, 147.7, 150.1, 152.9, 153.6, 153.7, 156.1, 164.5; MALDI-MS (dithranol) obsd 896.4 [(M−t-butyl)$^+$], 952.3 [M$^+$]; FAB-MS obsd 953.4997, calcd 953.5019; λ_{abs} 415, 531 nm; λ_{em} (λ_{ex}=500 nm) 571 nm. Anal. calcd for $C_{66}H_{67}NO_5$: C, 83.07; H, 7.08; N, 1.47; Found: C, 82.99; H, 7.42; N, 1.58.

4.3.4. 1,6,9-Tris(4-*tert*-butylphenoxy)-3,4-dicarboxylic anhydride (9). Following a standard procedure,[9,14] a mixture of **11** (6.90 g, 7.23 mmol) and KOH (21.0 g, 374 mmol) in 2-methyl-2-propanol (400 mL) was refluxed for 2 h, affording quantitative hydrolysis of the imide. The hot reaction mixture was poured into acetic acid (800 mL) and the mixture was vigorously stirred for 5 min at room temperature. To this mixture was added H_2O (1.0 L). The resulting precipitate was collected by vacuum filtration. The precipitate was washed with H_2O and dried in an oven at 130°C. TLC analysis [silica, CH_2Cl_2/hexanes (1:1)] showed the presence of a small amount of a magenta product (R_f=0.92, consistent with reformation of **11**) and the title compound (R_f=0.57, magenta). The crude solid was dissolved in CH_2Cl_2/hexanes [300 mL (1:3)] and vacuum filtered through a pad of silica (9.5×6.0 cm, swelled with hexanes) on a fritted glass filter. Elution with CH_2Cl_2/-hexanes [3.0 L (2:3)] removed a less polar byproduct, then CH_2Cl_2/hexanes [2.0 L (2:1)] eluted the title compound. The filtrate was concentrated to dryness. The solid was triturated with a small volume of methanol then filtered, affording a deep-purple solid (3.52 g, 63%): mp 152–154°C; ^{1}H NMR δ 1.33 (s, 9H), 1.35 (s, 9H), 1.36 (s, 9H), 6.87 (d, J=8.8 Hz, 1H), 6.99 (d, J=8.8 Hz, 2H), 7.05 (d, J=8.8 Hz, 2H), 7.10 (d, J=8.8 Hz, 2H), 7.39 (d, J=8.8 Hz, 2H), 7.42–7.45 (m, 4H), 7.61–7.67 (m, 1H), 8.14 (s, 1H), 8.17 (s, 1H), 8.52 (d, J=8.1 Hz, 1H), 9.23 (d, J=8.8 Hz, 1H), 9.43 (d, J=7.3 Hz, 1H); ^{13}C NMR δ 31.6, 34.6, 111.3, 115.5, 116.6, 118.6, 118.8, 120.3, 121.5, 124.8, 125.1, 125.4, 125.7, 126.7, 127.1, 127.3, 127.4, 127.5, 128.3, 128.6, 130.3, 130.7, 131.2, 147.6, 147.8, 148.0, 152.7, 153.2, 153.3, 153.6, 156.8, 160.1; MALDI-MS (dithranol) obsd 765.0 [M$^+$]; FAB-MS obsd 766.3315, calcd 766.3294; λ_{abs} 410, 533 nm; λ_{em} (λ_{ex}=500 nm) 578 nm. Anal. calcd for $C_{52}H_{46}O_6$: C, 81.44; H, 6.05; Found: C, 81.17; H, 6.19.

4.3.5. 2,6-Diisopropyl-4-[2-(triisopropylsilyl)ethynyl]-aniline (12d). Following a general procedure,[36] a mixture of **12c** (5.00 g, 16.5 mmol), $Pd(PPh_3)_2Cl_2$ (116 mg, 0.165 mmol) and CuI (31.4 mg, 0.165 mmol) was placed in a Schlenk flask then degassed triethylamine (50 mL) was added to the mixture. (Triisopropylsilyl)acetylene (4.50 mL, 20.1 mmol) was added and the mixture was stirred at room temperature for 16 h. The mixture was concentrated and taken up in ether. The resulting mixture was filtered and concentrated to dryness. Vacuum filtration through a pad of silica [9.5×6.0 cm, CH_2Cl_2/hexanes (4:1→2:1)] on a fritted glass filter afforded a faint yellow oil (5.20 g, 88%): ^{1}H NMR δ 1.17 (m, 18H), 1.29 (d, J=6.8 Hz, 12H), 2.86–2.92 (m, 2H), 3.93 (brs, 2H), 7.19 (s, 2H); ^{13}C NMR δ 11.4, 18.7, 22.2, 27.8, 86.6, 109.0, 112.7, 127.0, 132.0, 140.8; FAB-MS obsd 357.2845, calcd 357.2852. Anal. calcd for $C_{23}H_{39}NSi$: C, 77.24; H, 10.99; N, 3.92; Found: C, 77.17; H, 11.11; N, 3.96.

4.3.6. 2,6-Diisopropyl-4-[2-(trimethylsilyl)ethynyl]aniline (12e). Following a general procedure,[36] samples of **12c** (2.50 g, 8.25 mmol), $Pd(PPh_3)_2Cl_2$ (58.0 mg, 82.5 μmol) and CuI (15.7 mg, 82.5 μmol) were placed in a Schlenk flask, then degassed triethylamine (30 mL) was added to the mixture. (Trimethylsilyl)acetylene (1.28 mL, 9.08 mmol) was added and the mixture was stirred at room temperature for 16 h. The mixture was concentrated and taken up in ether. The resulting mixture was filtered and concentrated to dryness. Vacuum filtration through a pad of silica [6.0×6.0 cm, CH_2Cl_2/hexanes (3:1)] on a fritted glass filter afforded an orange oil that slowly crystallized (1.94 g, 86%): mp 69–72°C; ^{1}H NMR δ 0.24 (s, 9H), 1.24 (d, J=6.9 Hz, 12H), 2.83–2.88 (m, 2H), 3.89 (brs, 2H), 7.16 (s, 2H); ^{13}C NMR δ 0.2, 22.2, 27.7, 90.4, 107.2, 112.0, 126.9, 131.9, 141.1; FAB-MS obsd 273.1905, calcd 273.1913. Anal. calcd for $C_{17}H_{27}NSi$: C, 74.66; H, 9.95; N, 5.12; Found: C, 74.41; H, 9.90; N, 5.09.

4.3.7. 2,6-Diisopropyl-4-ethynylaniline (12f). A mixture of **12e** (1.40 g, 5.12 mmol) and TBAF on silica gel (7.68 g, ~1.1 mmol/g) in THF (120 mL) containing 0.1% water was stirred at room temperature for 1 h. TLC analysis (silica, $CHCl_3$) showed the complete removal of the trimethylsilyl group. The reaction mixture was washed with 10% aqueous $NaHCO_3$ and water, then dried over Na_2SO_4. Vacuum

filtration through a pad of silica [6.0×6.0 cm, CH_2Cl_2/hexanes (1:2)] on a fritted glass filter afforded an orange oil (629 mg, 61%): ^{1}H NMR δ 1.26 (d, J=6.4 Hz, 12H), 2.82–2.92 (m, 2H), 2.97 (s, 1H), 3.91 (brs, 2H), 7.19 (s, 2H); ^{13}C NMR δ 22.2, 27.8, 74.2, 85.5, 110.9, 127.1, 132.1, 141.3; FAB-MS obsd 201.1516, calcd 201.1517. Anal. calcd for $C_{14}H_{19}N$: C, 83.53; H, 9.51; N, 6.96; Found: C, 83.54; H, 9.54; N, 7.04.

4.3.8. Preparative-scale imidation procedure using DMF/Zn(OAc)$_2$·2H$_2$O, exemplified for 1,6,9-tris(4-*tert*-butylphenoxy)-*N*-(4-ethynylphenyl)perylene-3,4-dicarboximide (13a). Following a procedure modified from that of Langhals,[9] a mixture of **9** (3.25 g, 4.24 mmol), **12a** (1.49 g, 12.7 mmol, 3 equiv.), and $Zn(OAc)_2·2H_2O$ (850 mg, 3.87 mmol) in anhydrous DMF (100 mL) was stirred at 130°C for 17 h. TLC analysis [silica, CH_2Cl_2/hexanes (1:1)] showed the presence of the title compound (R_f=0.63, magenta), a small amount of **9** (R_f=0.58, magenta), a small amount of a byproduct (R_f=0.50, magenta), and the excess **12a** near the origin. The reaction mixture was cooled to room temperature and water (200 mL) was added. The resulting solid was collected by vacuum filtration on a fritted glass filter and washed with H_2O/methanol [300 mL (1:1)] to remove **12a**. The damp solid was dissolved in CH_2Cl_2 (300 mL). The solution was dried (Na_2SO_4), filtered, and the filtrate was concentrated to dryness. The crude solid was dissolved in toluene/hexanes [400 mL (1:1)] and vacuum filtered through a pad of silica [6.0×6.0 cm, swelled with toluene/hexanes (1:1)] on a fritted glass filter. Elution with toluene/hexanes [1.0 L (1:1)] removed a less polar byproduct, then toluene/hexanes [2.5 L (3:2)] eluted the title compound. The filtrate was concentrated to dryness. The solid was triturated with methanol then filtered, affording a magenta solid (1.84 g, 50%): mp >230°C; ^{1}H NMR δ 1.31 (s, 9H), 1.33 (s, 9H), 1.34 (s, 9H), 3.12 (s, 1H), 6.91 (d, J=8.8 Hz, 1H), 7.01 (d, J=8.8 Hz, 2H), 7.07 (d, J=8.1 Hz, 2H), 7.09 (d, J=8.8 Hz, 2H), 7.23–7.26 (overlapped with solvent peak, 2H), 7.36 (d, J=8.8 Hz, 2H), 7.41 (d, J=8.8 Hz, 2H), 7.42 (d, J=8.1 Hz, 2H), 7.60–7.68 (m, 3H), 8.24 (s, 1H), 8.27 (s, 1H), 8.49 (d, J=8.1 Hz, 1H), 9.28 (d, J=8.8 Hz, 1H), 9.48 (d, J=8.1 Hz, 1H); ^{13}C NMR δ 31.42, 31.44, 31.5, 78.0, 83.0, 111.7, 118.4, 118.6, 118.7, 119.8, 120.0, 121.0, 122.1, 122.5, 122.9, 124.1, 124.4, 125.8, 126.6, 126.9, 127.1, 127.2, 127.3, 127.4, 127.66, 127.68, 128.7, 129.9, 130.0, 130.6, 131.4, 133.0, 135.6, 147.1, 147.3, 147.5, 152.7, 153.36, 153.40, 153.5, 153.6, 156.1, 163.20, 163.22; MALDI-MS (dithranol) obsd 865.4 [M$^+$], 1013.5 [(M+148)$^+$]; FAB-MS obsd 865.3783, calcd 865.3767 ($C_{60}H_{51}NO_5$); λ_{abs} (log ε) 413 (3.8), 531 (4.6) nm; λ_{em} (λ_{ex}=500 nm) 574 nm.

4.3.9. Small-scale imidation procedure using imidazole/mesitylene/Zn(OAc)$_2$·2H$_2$O, exemplified for 1,6,9-tris(4-*tert*-butylphenoxy)-*N*-(2,6-diisopropylphenyl)perylene-3,4-dicarboximide (13b). Following a procedure modified from that of Langhals,[9] a mixture of **9** (50 mg, 65 μmol), 2,6-diisopropylaniline (247 μL, 1.30 mmol, 20 equiv.) and $Zn(OAc)_2·2H_2O$ (13 mg, 59 μmol) in imidazole (260 mg) and mesitylene (0.8 mL) was stirred at 130°C. After 19 h, the reaction mixture was cooled to room temperature and 2N aqueous HCl was added. The aqueous phase was extracted with CH_2Cl_2. The CH_2Cl_2 extracts were combined, dried (Na_2SO_4), and concentrated. The crude mixture obtained was purified by three silica column chromatography procedures [(1) toluene, (2) CH_2Cl_2/hexanes (2:3), and (3) toluene]. The desired fraction was concentrated to dryness. The resulting solid was treated with methanol and the mixture was centrifuged. The supernatant was decanted, leaving a magenta solid (24 mg, 40%): mp 174–176°C; ^{1}H NMR δ 1.14 (d, J=6.6 Hz, 12H), 1.32 (s, 9H), 1.34 (s, 9H), 1.35 (s, 9H), 2.66–2.76 (m, 2H), 6.90 (d, J=8.8 Hz, 1H), 7.02 (d, J=8.1 Hz, 2H), 7.08 (d, J=8.1 Hz, 2H), 7.10 (d, J=8.1 Hz, 2H), 7.29 (d, J=8.1 Hz, 2H), 7.37 (d, J=8.8 Hz, 2H), 7.39–7.46 (m, 5H), 7.62–7.67 (m, 1H), 8.30 (s, 1H), 8.34 (s, 1H), 8.48 (d, J=8.1 Hz, 1H), 9.25 (d, J=8.8 Hz, 1H), 9.45 (d, J=8.1 Hz, 1H); ^{13}C NMR δ 24.0, 29.0, 29.7, 31.5, 34.36, 34.39, 34.44, 111.6, 118.1, 118.2, 119.8, 120.5, 121.4, 122.1, 123.5, 123.9, 124.2, 124.7, 124.9, 125.8, 126.6, 126.9, 127.0, 127.1, 127.6, 127.7, 127.9, 129.3, 129.7, 129.8, 130.7, 130.8, 131.5, 145.6, 146.8, 147.0, 147.5, 152.4, 153.3, 153.4, 155.9, 163.2; MALDI-MS (dithranol) obsd 925.0 [M$^+$]; FAB-MS obsd 925.4718, calcd 925.4706 ($C_{64}H_{63}NO_5$); λ_{abs} (log ε) 412 (3.8), 533 (4.5) nm; λ_{em} (λ_{ex}=530 nm) 573, 622 (sh) nm.

4.3.10. 1,6,9-Tris(4-*tert*-butylphenoxy)-*N*-(2,6-diisopropyl-4-iodophenyl)perylene-3,4-dicarboximide (13c). Following the small-scale procedure used to prepare **13b**, a mixture of **9** (365 mg, 0.475 mmol), **12c** (434 mg, 1.43 mmol, 3 equiv.) and $Zn(OAc)_2·2H_2O$ (95.0 mg, 0.431 mmol) in imidazole (1.9 g) and mesitylene (3.0 mL) was stirred at 130°C. After 23 h, the reaction mixture was cooled to room temperature and 2N aqueous HCl was added. The aqueous phase was extracted with CH_2Cl_2. The CH_2Cl_2 extracts were combined, dried (Na_2SO_4), and concentrated. The crude mixture obtained was purified by column chromatography (silica, toluene). The desired fraction was concentrated to dryness. The solid was treated with methanol and the mixture was centrifuged. The supernatant was decanted, leaving a magenta solid (150 mg, 30%): mp >230°C; ^{1}H NMR δ 1.11 (d, J=6.6 Hz, 12H), 1.32 (s, 9H), 1.34 (s, 9H), 1.35 (s, 9H), 2.59–2.68 (m, 2H), 6.90 (d, J=8.8 Hz, 1H), 7.01 (d, J=8.1 Hz, 2H), 7.05–7.11 (m, 4H), 7.36 (d, J=8.1 Hz, 2H), 7.41 (d, J=8.8 Hz, 2H), 7.43 (d, J=8.1 Hz, 2H), 7.58 (s, 2H), 7.62–7.68 (m, 1H), 8.29 (s, 1H), 8.32 (s, 1H), 8.49 (d, J=8.8 Hz, 1H), 9.25 (d, J=8.8 Hz, 1H), 9.45 (d, J=8.1 Hz, 1H); ^{13}C NMR δ 24.0, 29.2, 31.7, 34.6, 96.3, 111.8, 118.3, 118.4, 120.0, 120.3, 121.3, 122.2, 123.8, 124.6, 125.0, 126.0, 126.8, 127.1, 127.3, 127.8, 128.0, 128.3, 130.0, 130.2, 130.9, 131.2, 131.8, 133.7, 147.1, 147.3, 147.8, 148.4, 152.6, 153.5, 153.6, 156.3, 163.3; MALDI-MS (dithranol) obsd 1050.6 [M$^+$], 925.9 [(M−I)$^+$]; FAB-MS obsd 1051.3680, calcd 1051.3673 ($C_{64}H_{62}INO_5$); λ_{abs} (log ε) 413 (3.6), 537 (4.5) nm; λ_{em} (λ_{ex}=500 nm) 577, 623 (sh) nm.

4.3.11. Preparative-scale imidation procedure using imidazole/mesitylene/Zn(OAc)$_2$·2H$_2$O, exemplified for 1,6,9-tris(4-*tert*-butylphenoxy)-*N*-[2,6-diisopropyl-4-[2-(triisopropylsilyl)ethynyl]phenyl]-3,4-perylenedicarboximide (13d). Following a procedure modified from that of Langhals,[9] a mixture of **9** (1.00 g, 1.30 mmol), **12d** (9.32 g, 26.1 mmol) and $Zn(OAc)_2·2H_2O$ (280 mg, 1.28 mmol) in imidazole (5.2 g) and mesitylene (16 mL)

was stirred at 130°C. After 22 h, $Zn(OAc)_2{\cdot}2H_2O$ (280 mg, 1.28 mmol) was added. After 14 h (total 36 h), the reaction mixture was cooled to room temperature and extracted with CH_2Cl_2. The organic phase was washed with 2N aqueous HCl and water, dried (Na_2SO_4), and concentrated. TLC analysis [silica, CH_2Cl_2/hexanes (1:1)] showed the presence of the title compound (R_f=0.70, magenta), unreacted **12d** (R_f=0.55, colorless), a small amount of byproduct (R_f=0.32, colorless), and a small amount of starting material **9** (R_f=0.29, purple). The residue was diluted with CH_2Cl_2/hexanes [100 mL (1:4)] and vacuum filtered through a pad of silica [9.5×6.0 cm, swelled with CH_2Cl_2/hexanes (1:4)] on a fritted glass filter. The byproduct was removed by eluting with CH_2Cl_2/hexanes [1.0 L, (1:4), fraction 1] and the desired product was eluted with CH_2Cl_2/hexanes [1.0 L, (1:4), fraction 2], then the mixture of the desired compound and excess **12d** was eluted with CH_2Cl_2/hexanes [1.0 L, (1:2), fraction 3]. Fractions 2 and 3 were combined and concentrated to dryness. The solid was triturated with methanol followed by filtration, affording a magenta solid (687 mg, 48%): mp >230°C; ^{1}H NMR δ 1.12–1.15 (m, 33H), 1.32 (s, 9H), 1.337 (s, 9H), 1.342 (s, 9H), 2.64–2.73 (m, 2H), 6.88 (d, J=8.8 Hz, 1H), 7.00 (d, J=8.8 Hz, 2H), 7.05–7.10 (m, 4H), 7.35–7.43 (m, 8H), 7.60–7.66 (m, 1H), 8.30 (s, 1H), 8.33 (s, 1H), 8.47 (d, J=8.1 Hz, 1H), 9.23 (d, J=8.8 Hz, 1H), 9.43 (d, J=7.3 Hz, 1H); ^{13}C NMR δ 11.5, 18.9, 24.0, 29.2, 31.7, 34.6, 107.7, 111.8, 118.2, 118.4, 120.0, 120.5, 121.5, 122.3, 123.8, 124.5, 124.7, 125.1, 125.3, 126.0, 126.8, 127.1, 127.3, 127.9, 128.0, 128.1, 128.3, 130.0, 130.1, 131.0, 131.8, 146.1, 147.1, 147.2, 152.6, 153.4, 153.6, 156.3, 163.3; MALDI-MS (dithranol) obsd 1105.3 [M^+]; FAB-MS obsd 1105.6045, calcd 1105.6041 ($C_{75}H_{83}NO_5Si$); λ_{abs} (log ε) 415 (3.9), 536 (4.6) nm; λ_{em} (λ_{ex}=500 nm) 576, 622 (sh) nm. The filtrate generated from trituration with methanol was concentrated and dried in vacuo followed by bulb-to-bulb distillation (170°C, 0.01 mm Hg), affording **12d** as a faint orange oil (5.04 g, 54% recovery).

4.3.12. 1,6,9-Tris(4-*tert*-butylphenoxy)perylene-3,4-dicarboxylic anhydride (9): conversion from 13a. Following a standard procedure,[9,14] a mixture of **13a** (500 mg, 580 μmol) and KOH (1.66 g, 29.6 mmol) in 2-methyl-2-propanol (35 mL) was refluxed for 2 h. The resulting hot solution was poured into acetic acid (70 mL) and the reaction mixture was vigorously stirred for 5 min. Water (100 mL) was added and the precipitate formed was collected by filtration. The crude solid was washed with water and a small amount of methanol (~5 mL). After drying in vacuo, the solid was dissolved in CH_2Cl_2/hexanes [10 mL (1:3)] and vacuum filtered through a pad of silica (6.0×6.0 cm, swelled with hexanes) on a fritted glass filter. A byproduct was removed by eluting with CH_2Cl_2/hexanes (2:3), then the desired product was obtained by elution with CH_2Cl_2/hexanes (2:1). The collected fractions were concentrated to dryness and the resulting solid was triturated with methanol, affording a deep-purple solid (398 mg, 90%). Characterization data were identical to those described above.

4.3.13. 1,6,9-Tris(4-*tert*-butylphenoxy)-*N*-(2,6-diisopropyl-4-ethynylphenyl)-3,4-perylenedicarboximide (4). A sample of **13d** (640 mg, 0.578 mmol) was treated with TBAF (694 μL, 0.694 mmol, 1.0 M solution in THF) in THF (30 mL) at room temperature for 30 min. The reaction mixture was extracted with CH_2Cl_2 and the organic phase was washed with saturated $NaHCO_3$ and water, dried over Na_2SO_4, then concentrated. TLC analysis [CH_2Cl_2/hexanes (1:1)] showed the title compound (R_f=0.61, magenta) and a small amount of byproduct (R_f=0.50, purple). The resulting residue was dissolved in toluene/hexanes [100 mL, (1:1)] and vacuum filtered through a pad of silica [9.5×6.0 cm, swelled with toluene/hexanes (1:1)] on a fritted glass filter. A byproduct was removed by eluting with toluene/hexanes [1.5 L, (1:1)] and the desired product was eluted with toluene/hexanes [2.0 L, (3:2)]. The product fractions were combined and concentrated. The resulting solid was triturated with methanol, affording a magenta solid (441 mg, 88%). Characterization data were identical to those in the literature.[7]

4.3.14. 3,5-Bis[2-[4-[1,6,9-tris(4-*tert*-butylphenoxy)perylene-3,4-dicarboximido]-3,5-disopropylphenyl]ethynyl]-benzaldehyde (20). Following a standard procedure,[20] a mixture of **13c** (100 mg, 95.0 μmol), 3,5-diethynylbenzaldehyde (**19**, 6.2 mg, 40 μmol), $Pd_2(dba)_3$ (8.7 mg, 9.5 μmol), and P(*o*-tol)$_3$ (23 mg, 76 μmol) in toluene/triethylamine [8.0 mL (5:1)] was stirred under argon at 40°C. After 2 h, the reaction mixture was loaded onto a silica column and eluted with toluene followed by trituration with methanol, affording a magenta solid (34 mg, 42%). Characterization data were identical to those in the literature.[20]

4.3.15. 3,5-Bis[2-[4-[9-(4-*tert*-butylphenoxy)perylene-3,4-dicarboximido]-3,5-diisopropylphenyl]ethynyl]-phenyl]benzaldehyde (21). Following a slightly modified procedure,[20] a mixture of **5** (232 mg, 355 μmol), 3,5-dibromobenzaldehyde (**18**, 39.0 mg, 148 μmol), $Pd_2(dba)_3$ (27.0 mg, 29.7 μmol), and P(*o*-tol)$_3$ (54.0 mg, 178 μmol) in toluene/triethylamine [25 mL (10:1)] was stirred at 60°C under argon. After 3 h, another identical batch of catalyst was added. After 18 h, the mixture was cooled and passed through a silica column [$CHCl_3$/ethyl acetate (9:1)]. Two column chromatography procedures [silica, $CHCl_3$/ethyl acetate (95:5) and (98:2)] afforded a red solid (74.0 mg, 35%): mp >230°C; ^{1}H NMR δ 1.22 (d, J=6.6 Hz, 24H), 1.38 (s, 18H), 2.74–2.81 (m, 4H), 6.99 (d, J=8.8 Hz, 2H), 7.14 (d, J=8.8 Hz, 4H), 7.48 (d, J=8.8 Hz, 4H), 7.54 (m, 4H), 7.71–7.76 (m, 2H), 8.05 (m, 3H), 8.35 (d, J=8.1 Hz, 2H), 8.39 (d, J=8.8 Hz, 2H), 8.49 (d, J=8.1 Hz, 2H), 8.51 (d, J=7.3 Hz, 2H), 8.60 (d, J=7.3 Hz, 2H), 8.65 (d, J=8.1 Hz, 2H), 8.69 (d, J=8.1 Hz, 2H), 10.07 (s, 1H); MALDI-MS (dithranol) obsd 1409.4 [M^+], calcd avg mass 1409.7 ($C_{99}H_{80}N_2O_7$); λ_{abs} 510 nm; λ_{em} (λ_{ex}=510 nm) 570, 614, 671 (sh) nm.

4.3.16. 3,5-Bis[2-[4-[1,6,9-tris(4-*tert*-butylphenoxy)perylene-3,4-dicarboximido]phenyl]ethynyl]benzaldehyde (22). Following a standard procedure,[20] a mixture of **13a** (700 mg, 864 μmol), 3,5-dibromobenzaldehyde (**18**, 95.0 mg, 360 μmol), $Pd_2(dba)_3$ (33.0 mg, 36.0 μmol), PPh_3 (57.0 mg, 217 μmol), and CuI (17.0 mg, 89.2 μmol) in toluene/triethylamine [72 mL (5:1)] was stirred under argon at 50°C. After 3 h, another identical batch of catalyst was added. After 20 h, the reaction mixture was cooled to room

temperature and then passed through a silica column [$CHCl_3$/hexanes (4:1)]. The resulting residue was further purified by preparative SEC (THF) followed by column chromatography [silica, $CHCl_3$/hexanes (9:1)] to yield a magenta solid (457 mg, 69%): ^{1}H NMR δ 1.31 (s, 18H), 1.34 (s, 18H), 1.35 (s, 18H), 6.85 (d, J=8.8 Hz, 2H), 7.00 (d, J=8.8 Hz, 4H), 7.06 (d, J=8.8 Hz, 4H), 7.10 (d, J=8.8 Hz, 4H), 7.27 (d, J=8.8 Hz, 4H), 7.36 (d, J=8.8 Hz, 4H), 7.40–7.43 (m, 8H), 7.57–7.62 (m, 4H), 7.64 (d, J=8.8 Hz, 4H), 7.91–7.96 (m, 3H), 8.18 (s, 2H), 8.21 (s, 2H), 8.45 (d, J=8.4 Hz, 2H), 9.20 (d, J=8.8 Hz, 2H), 9.41 (d, J=8.0 Hz, 2H), 9.98 (s, 1H); ^{13}C NMR δ 29.4, 29.7, 31.43, 31.45, 31.5, 34.37, 34.41, 34.44, 87.8, 91.0, 111.5, 118.4, 118.6, 119.8, 119.9, 120.8, 121.9, 122.7, 122.8, 124.0, 124.2, 124.7, 125.6, 126.4, 126.9, 127.07, 127.14, 127.3, 127.5, 127.6, 129.0, 129.7, 129.8, 130.4, 131.2, 132.0, 132.4, 135.5, 136.5, 139.5, 147.0, 147.2, 147.5, 152.6, 153.4, 155.9, 163.1, 190.7; MALDI-MS (POPOP) obsd 1834.3 [M^+], calcd avg mass 1834.2 ($C_{127}H_{104}N_2O_{12}$); λ_{abs} 415, 533; λ_{em} (λ_{ex}=420 nm) 575, 625 (sh) nm.

4.3.17. 5-[3,5-Bis[2-[4-[1,6,9-tris(4-*tert*-butylphenoxy)-perylene-3,4-dicarboximido]phenyl]ethynyl]phenyl]dipyrromethane (23). Following a standard procedure[29] with slight modification,[21] a solution of **22** (500 mg, 273 μmol) in CH_2Cl_2 (2.7 mL) was treated with pyrrole (8.0 mL, 0.11 mol) followed by TFA (2.1 μL, 27 μmol). The mixture was stirred at room temperature. After 15 min, triethylamine (2 mL) and CH_2Cl_2 (20 mL) were added. The reaction mixture was washed with brine, dried over Na_2SO_4 and purified by column chromatography (silica, $CHCl_3$), affording a magenta solid (510 mg, 96%): ^{1}H NMR δ 1.32 (s, 18H), 1.34 (s, 18H), 1.35 (s, 18H), 5.48 (s, 1H), 5.95–5.98 (m, 2H), 6.19 (dd, J^1=4.4 Hz, J^2=2.4 Hz, 2H), 6.26 (dd, J^1=4.4 Hz, J^2=2.4 Hz, 1H), 6.83 (dd, J^1=4.4 Hz, J^2=2.4 Hz, 1H), 6.89 (d, J=9.2 Hz, 4H), 7.00 (d, J=8.8 Hz, 4H), 7.06 (d, J=9.2 Hz, 4H), 7.09 (d, J=8.8 Hz, 4H), 7.26 (d, J=8.8 Hz, 4H), 7.36 (d, J=8.8 Hz, 4H), 7.39–7.44 (m, 9H), 7.62 (d, J=8.8 Hz, 4H), 7.64–7.65 (m, 2H), 8.01 (brs, 2H), 8.21 (s, 2H), 8.23 (s, 2H), 8.48 (dd, J^1=8.0 Hz, J^2=1.2 Hz, 2H), 9.25 (d, J=8.8 Hz, 2H), 9.25 (d, J=8.8 Hz, 2H), 9.44 (dd, J^1=8.0 Hz, J^2=1.2 Hz, 2H); ^{13}C NMR δ 29.7, 31.43, 31.45, 31.5, 34.38, 34.41, 34.44, 43.6, 89.2, 89.7, 107.6, 108.6, 111.6, 117.7, 118.4, 118.6, 119.8, 120.0, 120.9, 122.1, 122.8, 123.3, 123.7, 124.1, 124.3, 125.8, 126.5, 126.9, 127.09, 127.15, 127.3, 127.57, 127.63, 128.8, 129.8, 129.9, 130.5, 130.9, 131.3, 131.5, 132.0, 132.4, 133.5, 135.2, 142.8, 147.1, 147.2, 147.5, 152.7, 153.37, 153.40, 153.45, 153.54, 156.0, 163.2; MALDI-MS (dithranol) obsd 1950.7 [M^+], calcd avg mass 1950.4 ($C_{135}H_{112}N_4O_2$); λ_{abs} 414, 531 nm; λ_{em} (λ_{ex}=540 nm) 574, 621 (sh) nm.

4.3.18. 5-[3,5-Bis[2-[4-[1,6,9-tris(4-*tert*-butylphenoxy)-perylene-3,4-dicarboximido]phenyl]ethynyl]phenyl]-10-(4-ethynylphenyl)-20-(4-iodophenyl)-15-mesitylporphinatozinc(II) (16). Following a standard procedure[28] with improved acid catalysis conditions,[31] a sample of **24** (112 mg, 179 μmol) was reduced with $NaBH_4$ (136 mg, 3.60 mmol) in THF/methanol [20 mL (10:1)]. The resulting dipyrromethane–dicarbinol (**24**-diol) was condensed with **23** (344 mg, 179 μmol) in CH_2Cl_2 (7.0 mL) in the presence of $Yb(OTf)_3$ (145 mg, 234 μmol) at room temperature. After 30 min, DDQ (123 mg, 542 μmol) was added and the mixture was stirred at room temperature for 1 h. Triethylamine was added to the reaction mixture and the resulting mixture was filtered through a silica column [CH_2Cl_2/hexanes (2:1)]. The resulting residue was dissolved in CH_2Cl_2 (40 mL) and the mixture was treated with a solution of $Zn(OAc)_2{\cdot}2H_2O$ (201 mg, 917 μmol) in methanol (10 mL) at room temperature. After 15 h, the mixture was washed with water, dried (Na_2SO_4), then chromatographed [silica, CH_2Cl_2/hexanes (2:1)]. The desired fraction was collected and concentrated. The resulting solid was treated with methanol and the suspension was sonicated for 10–20 s. Filtration afforded a red solid (45 mg, 10%): ^{1}H NMR δ 1.28 (s, 18H), 1.30 (s, 18H), 1.34 (s, 18H), 1.84 (s, 6H), 2.64 (s, 3H), 3.31 (s, 1H), 6.89 (d, J=9.2 Hz, 2H), 7.00 (d, J=8.4 Hz, 4H), 7.05–7.10 (m, 8H), 7.26–7.29 (m, 6H), 7.35 (d, J=8.8 Hz, 4H), 7.40 (d, J=8.8 Hz, 4H), 7.41 (d, J=8.8 Hz, 4H), 7.58–7.65 (m, 2H), 7.68 (d, J=8.4 Hz, 4H), 7.84–7.93 (m, 4H), 8.05 (d, J=8.0 Hz, 2H), 8.15 (d, J=8.8 Hz, 2H), 8.18–8.19 (m, 1H), 8.22 (s, 2H), 8.24 (s, 2H), 8.37–8.38 (m, 2H), 8.47 (d, J=8.4 Hz, 2H), 8.81 (d, J=4.8 Hz, 2H), 8.87 (d, J=4.4 Hz, 2H), 8.91–8.92 (m, 2H), 8.99 (d, J=4.8 Hz, 2H), 9.25 (d, J=8.8 Hz, 2H), 9.45 (d, J=8.4 Hz, 2H); MALDI-MS (dithranol) obsd 2597.2 [M^+], calcd avg mass 2598.2 ($C_{169}H_{131}IN_6O_{10}Zn$); λ_{abs} 427 (fwhm=13 nm), 535 nm; λ_{em} (λ_{ex}=540 nm) 598, 646 nm.

4.3.19. 5-[3,5-Bis[2-[4-[1,6,9-tris(4-*tert*-butylphenoxy)-perylene-3,4-dicarboximido]phenyl]ethynyl]phenyl]-10,20-bis(4-ethynylphenyl)-15-mesitylporphinatozinc(II) (17). Following a standard procedure[28] with improved acid catalysis conditions,[31] a sample of **25** (54.0 mg, 103 μmol) was reduced with $NaBH_4$ (78.0 mg, 2.05 mmol) in THF/methanol [5 mL (10:1)]. The resulting dipyrromethane–dicarbinol (**25**-diol) was reacted with **23** (200 mg, 103 μmol) in CH_2Cl_2 (40 mL) in the presence of $Yb(OTf)_3$ (83.0 mg, 134 μmol) at room temperature. After 20 min, the reaction mixture was treated with DDQ (70.0 mg, 308 μmol) and stirred for 1 h. Triethylamine was then added and the mixture was filtered through a silica column [CH_2Cl_2/hexanes (2:1)]. The resulting residue was dissolved in $CHCl_3$ (20 mL) and the mixture was treated with a solution of $Zn(OAc)_2{\cdot}2H_2O$ (113 mg, 513 μmol) in methanol (5.0 mL) at room temperature. After 2 h, the mixture was washed with water, dried (Na_2SO_4) and chromatographed [silica, CH_2Cl_2/hexanes (2:1)] affording a red solid (30 mg, 31%): ^{1}H NMR δ 0.99 (s, 18H), 1.01 (s, 18H), 1.21 (s, 18H), 1.84 (s, 6H), 2.31 (s, 2H), 2.96–2.98 (m, 3H), 6.57 (d, J=9.2 Hz, 2H), 6.67 (d, J=8.8 Hz, 4H), 6.72–6.77 (m, 6H), 6.93–7.09 (m, 12H), 7.31 (d, J=7.6 Hz, 4H), 7.36 (d, J=7.6 Hz, 4H), 7.50–7.54 (m, 5H), 7.83–7.84 (m, 4H), 7.90 (d, J=10.0 Hz, 4H), 8.05 (s, 2H), 8.15 (d, J=8.0 Hz, 4H), 8.49–8.67 (m, 12H), 8.93 (d, J=8.8 Hz, 2H), 9.13 (d, J=7.6 Hz, 2H), 9.68 (s, 2H); MALDI-MS (dithranol) obsd 2497.5 [$(M+H)^+$], calcd avg mass 2496.3 ($C_{171}H_{132}N_6O_{10}Zn$); λ_{abs} 427 (fwhm=13 nm), 536 nm; λ_{em} (λ_{ex}=540 nm) 598, 647 nm.

4.3.20. Sonogashira oligomerization of 16. Following a standard procedure,[21] a mixture of **16** (20 mg, 7.7 μmol), $Pd_2(dba)_3$ (1.1 mg, 1.2 μmol) and $AsPh_3$ (2.8 mg, 9.2 μmol) in toluene/triethylamine [3 mL (5:1)] was stirred under argon at room temperature for 40 h. The reaction

mixture was heterogeneous. The bis(perylene)porphyrin precipitate afforded a very dilute solution in THF upon sonication at room temperature. Due to the low solubility of the material, further purification and analysis were not attempted.

4.3.21. Glaser oligomerization of 17. Following a standard procedure,[21,37] a mixture of **17** (25 mg, 10 μmol), $Pd(PPh_3)_2Cl_2$ (1.4 mg, 2.0 μmol) and CuI (0.38 mg, 2.0 μmol) in toluene/DIEA [4 mL (5:1)] was stirred at room temperature for 3 h. The reaction mixture appeared to be slightly opaque suggesting the formation of some precipitate. Analysis of a reaction sample by SEC indicated the presence of a considerable amount (about 40%) of high molecular weight material with little starting monomer and short oligomers. The reaction mixture was concentrated to dryness. The resulting residue was dissolved in THF and the mixture was passed through a preparative SEC column (THF). The leading band was collected and concentrated to dryness. The resulting solid was triturated with methanol and then filtered, then the filtered material was triturated with hexanes and filtered, affording a red solid (8.2 mg, 33%): λ_{abs} 437, 507, 548; λ_{em} (λ_{ex}=450 nm) 607, 654 nm. A ^{1}H NMR spectrum was collected but the peaks were quite broad, indicative of aggregation. Due to the low solubility of the material, further analysis was not attempted.

4.3.22. 5,15-Bis[3,5-bis[2-[4-[1,6,9-tris(4-*tert*-butylphenoxy)perylene-3,4-dicarboximido]phenyl]ethynyl]phenyl]-10,20-dimesitylporphinatozinc(II) (27). Following a standard procedure,[20,32] a mixture of **22** (50 mg, 27 μmol) and **26** (7.2 mg, 27 μmol) in CH_2Cl_2 (2.5 mL) was treated with TFA (3.7 μL, 48 μmol) at room temperature for 30 min. DDQ (9.3 mg, 41 μmol) was then added and the reaction mixture was stirred for 1 h. After triethylamine was added, the crude mixture was passed through a silica column [CH_2Cl_2/hexanes (3:1)]. The resulting porphyrin was treated with $Zn(OAc)_2{\cdot}2H_2O$ (15 mg, 69 μmol) in $CHCl_3$/methanol [10 mL (4:1)] at room temperature for 12 h. The reaction mixture was washed with water, dried over Na_2SO_4 and then chromatographed [silica, $CHCl_3$/hexanes (3:1)]. The desired fraction was concentrated to dryness. Methanol was added and the suspension was sonicated for 10–20 s. Filtration afforded a red solid (5.0 mg, 8.8%): ^{1}H NMR δ 1.29 (s, 36H), 1.32 (s, 36H), 1.34 (s, 36H), 1.84 (s, 12H), 2.64 (s, 6H), 6.90 (d, *J*=8.8 Hz, 4H), 6.99 (d, *J*=8.8 Hz, 8H), 7.05 (d, *J*=8.8 Hz, 8H), 7.08 (d, *J*=8.8 Hz, 8H), 7.25–7.29 (m, 8H), 7.35 (d, *J*=8.8 Hz, 8H), 7.39 (d, *J*=8.8 Hz, 8H), 7.42 (d, *J*=8.8 Hz, 8H), 7.64 (m, 8H), 7.68 (d, *J*=8.4 Hz, 8H), 8.16 (s, 2H), 8.22 (d, *J*=7.6 Hz, 8H), 8.39–8.40 (m, 4H), 8.48 (d, *J*=8.8 Hz, 4H), 8.82 (d, *J*=4.4 Hz, 4H), 8.93 (d, *J*=4.4 Hz, 4H), 9.26 (d, *J*=8.8 Hz, 4H), 9.46 (d, *J*=8.8 Hz, 4H); MALDI-MS (dithranol) obsd 4212.89 [$(M+H)^+$], calcd avg mass 4218.41 ($C_{290}H_{236}N_8O_{20}Zn$); λ_{abs} 427 (fwhm=13 nm), 534 nm; λ_{em} (λ_{ex}=540 nm) 596, 646 nm.

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References

1. Zollinger, H. *Color Chemistry*; 2nd ed. VCH: Weinheim, 1991.
2. O'Neil, M. P.; Niemczyk, M. P.; Svec, W. A.; Gosztola, D.; Gaines, G. L. III; Wasielewski, M. R. *Science* **1992**, *257*, 63–65.
3. Prathapan, S.; Yang, S. I.; Seth, J.; Miller, M. A.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Phys. Chem. B* **2001**, *105*, 8237–8248.
4. Yang, S. I.; Prathapan, S.; Miller, M. A.; Seth, J.; Bocian, D. F.; Lindsey, J. S.; Holten, D. *J. Phys. Chem. B* **2001**, *105*, 8249–8258.
5. Yang, S. I.; Lammi, R. K.; Prathapan, S.; Miller, M. A.; Seth, J.; Diers, J. R.; Bocian, D. F.; Lindsey, J. S.; Holten, D. *J. Mater. Chem.* **2001**, *11*, 2420–2430.
6. Kirmaier, C.; Yang, S. I.; Prathapan, S.; Miller, M. A.; Diers, J. R.; Bocian, D. F.; Lindsey, J. S.; Holten, D. *Res. Chem. Intermed.* **2002**, *28*, 719–740.
7. Loewe, R. S.; Tomizaki, K.-Y.; Chevalier, F.; Lindsey, J. S. *J. Porphyrins Phthalocyanines* **2003**, In press.
8. Gosztola, D.; Niemczyk, M. P.; Svec, W.; Lukas, A. S.; Wasielewski, M. R. *J. Phys. Chem. A* **2000**, *104*, 6545–6551.
9. Feiler, L.; Langhals, H.; Polborn, K. *Liebigs Ann.* **1995**, 1229–1244.
10. Quante, H.; Müllen, K. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1323–1325.
11. Holtrup, F. O.; Müller, G. R. J.; Quante, H.; De Feyter, S.; De Schryver, F. C.; Müllen, K. *Chem. Eur. J.* **1997**, *3*, 219–225.
12. Müller, G. R. J.; Meiners, C.; Enkelmann, V.; Geerts, Y.; Müllen, K. *J. Mater. Chem.* **1998**, *8*, 61–64.
13. (a) Gensch, T.; Hofkens, J.; Heirmann, A.; Tsuda, K.; Verheijen, W.; Vosch, T.; Christ, T.; Basché, T.; Müllen, K.; De Schryver, F. C. *Angew. Chem. Int. Ed.* **1999**, *38*, 3752–3756. (b) Hofkens, J.; Latterini, L.; De Belder, G.; Gensch, T.; Maus, M.; Vosch, T.; Karni, Y.; Schweitzer, G.; De Schryver, F. C.; Hermann, A.; Müllen, K. *Chem. Phys. Lett.* **1999**, *304*, 1–9. (c) Gronheid, R.; Hofkens, J.; Köhn, F.; Weil, T.; Reuther, E.; Müllen, K.; De Schryver, F. C. *J. Am. Chem. Soc.* **2002**, *124*, 2418–2419.
14. Gosztola, D.; Niemczyk, M. P.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1998**, *120*, 5118–5119.
15. Fuller, M. J.; Wasielewski, M. R. *J. Phys. Chem. B* **2001**, *105*, 7216–7219.
16. Just, E. M.; Wasielewski, M. R. *Superlatt. Microstruct.* **2000**, *28*, 317–328.
17. Hayes, R. T.; Wasielewski, M. R.; Gosztola, D. *J. Am. Chem. Soc.* **2000**, *122*, 5563–5567.
18. Lukas, A. S.; Zhao, Y.; Miller, S. E.; Wasielewski, M. R. *J. Phys. Chem. B* **2002**, *106*, 1299–1306.
19. (a) Miller, M. A.; Lammi, R. K.; Prathapan, S.; Holten, D.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 6634–6649. (b) Ambroise, A.; Kirmaier, C.; Wagner, R. W.; Loewe,

R. S.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Org. Chem.* **2002**, *67*, 3811–3826.
20. Tomizaki, K.-Y.; Loewe, R. S.; Kirmaier, C.; Schwartz, J. K.; Retsek, J. L.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Org. Chem.* **2002**, *67*, 6519–6534.
21. Loewe, R. S.; Tomizaki, K.-Y.; Youngblood, W. J.; Bo, Z.; Lindsey, J. S. *J. Mater. Chem.* **2002**, *12*, 3438–3451.
22. (a) Langhals, H. *Nachr. Chem. Tech. Lab.* **1980**, *28*, 716–718. (b) Rademacher, A.; Märkle, S.; Langhals, H. *Chem. Ber.* **1982**, *115*, 2927–2934. (c) Langhals, H.; Ismael, R.; Yürük, O. *Tetrahedron* **2000**, *56*, 5435–5441.
23. Langhals, H. *Chem. Ber.* **1985**, *118*, 4641–4645.
24. Böhm, A.; Helfer, W. US 5,808,073.
25. (a) Langhals, H.; Demmig, S.; Huber, H. *Spectrochim. Acta* **1988**, *44A*, 1189–1193. (b) Adachi, M.; Murata, Y.; Nakamura, S. *J. Phys. Chem.* **1995**, *99*, 14240–14246.
26. (a) Vogel, A. *Vogel's Textbook of Practical Organic Chemistry, including Quantitative Organic Analysis*; 4th ed. Longman: New York, 1978; revised by Furniss, B. S.; Hannaford, A. J.; Roger, V.; Smith, P. W. G.; Tatchell, A. R., p 909. (b) Knox, J. R.; Toia, R. F.; Casida, J. E. *J. Agric. Food Chem.* **1992**, *40*, 909–913.
27. Demmig, S.; Langhals, H. *Chem. Ber.* **1988**, *121*, 225–230.
28. Rao, P. D.; Dhanalekshimi, S.; Littler, B. J.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 7323–7344.
29. Littler, B. J.; Miller, M. A.; Hung, C.-H.; Wagner, R. W.; O'Shea, D. F.; Boyle, P. D.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 1391–1396.
30. Li, F.; Yang, S. I.; Ciringh, Y.; Seth, J.; Martin, C. H. III; Singh, D. L.; Kim, D.; Birge, R. R.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Am. Chem. Soc.* **1998**, *120*, 10001–10017.
31. Geier, G. R. III; Callinan, J. B.; Rao, P. D.; Lindsey, J. S. *J. Porphyrins Phthalocyanines* **2001**, *5*, 810–823.
32. Littler, B. J.; Ciringh, Y.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 2864–2872.
33. del Rosario Benites, M.; Johnson, T. E.; Weghorn, S.; Yu, L.; Rao, P. D.; Diers, J. R.; Yang, S. I.; Kirmaier, C.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Mater. Chem.* **2002**, *12*, 65–80.
34. Wagner, R. W.; Ciringh, Y.; Clausen, C.; Lindsey, J. S. *Chem. Mater.* **1999**, *11*, 2974–2983.
35. Tomizaki, K.-Y.; Yu, L.; Lindsey, J. S. Unpublished data.
36. Lavastre, O.; Ollivier, L.; Dixneuf, P. H.; Sibandhit, S. *Tetrahedron* **1996**, *52*(15), 5495–5505.
37. Liu, Q.; Burton, D. J. *Tetrahedron Lett.* **1997**, *38*, 4371–4374.