JOURNAL OF Materials CHEMISTRY

Synthesis of perylene–porphyrin building blocks and rod-like oligomers for light-harvesting applications†

Robert S. Loewe, Kin-ya Tomizaki, W. Justin Youngblood, Zhishan Bo and Jonathan S. Lindsey*

Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204, USA.
E-mail: jlindsey@ncsu.edu

Received 12th June 2002, Accepted 15th August 2002
First published as an Advance Article on the web 7th October 2002

We present the synthesis of four perylene–porphyrin building blocks for use in Glaser, Sonogashira, or Suzuki polymerizations. The building blocks bear synthetic handles (4-ethynylphenyl, 4-iodophenyl, bromo) at the *trans* (5,15) *meso*-positions of a zinc porphyrin and contain two or four perylene-monoimide dyes attached at the 3,5-positions of the non-linking *meso*-aryl rings of the porphyrin. Each perylene-monoimide bears three 4-*tert*-butylphenoxy substituents (at the 1-, 6-, and 9-positions) and two isopropyl groups (on the *N*-aryl unit) for increased solubility. In each case the intervening linker is a diarylethyne unit that bridges the *N*-imide position of the perylene and the *meso*-position of the porphyrin. The perylene–porphyrin building blocks were prepared by (1) reaction of a diperylene-dipyrromethane with an aldehyde yielding a *trans*-A_2B_2-porphyrin, (2) reaction of a diperylene-aldehyde with a dipyrromethane yielding a *trans*-A_2B_2-porphyrin, and (3) reaction of a diperylene-dipyrromethane with a dipyrromethane-dicarbinol yielding a *trans*-AB_2C-porphyrin or ABCD-porphyrin. The building blocks were subjected to Glaser, Sonogashira, or Suzuki coupling conditions in an effort to prepare oligomers containing porphyrins joined *via* 4,4′-diphenylbutadiyne (dpb), 4,4′-diphenylethyne (dpe), or 1,4-phenylene linkers (p), respectively. Each porphyrin in the backbone bears two or four pendant perylene-monoimide dyes. The Glaser and Sonogashira reactions afforded a distribution of oligomers, whereas the Suzuki reaction was unsuccessful. The oligomers were soluble in solvents such as toluene, THF, or $CHCl_3$ enabling routine handling. The use of perylenes results in (1) increased light-harvesting efficiency particularly in the green spectral region where porphyrins are relatively transparent and (2) greater solubility than is achieved with the use of porphyrins alone. The soluble perylene–porphyrin oligomers are attractive for use as light-harvesting materials in molecular-based solar cells.

Introduction

Light-harvesting rods that absorb intensely across the visible spectrum and funnel the resulting excited-state energy to one end of the rod may find use in molecular-based solar cells.[1] A number of general challenges must be met before effective light-harvesting rods of this type become accessible. The challenges include (1) incorporating pigments with absorption spectra that match the solar spectrum, (2) achieving appropriate electronic coupling of the pigments, and (3) developing molecular designs wherein the rods and precursors to the rods have sufficient solubility for routine processing. A general approach toward such rods employs the polymerization of photoactive monomers.

A wide variety of polymers bearing pendant chromophores have been prepared and their energy-transfer properties have been characterized.[2–4] The approach we have employed has focused on discrete arrays containing porphyrins embedded in the backbone of the array *via* covalent linkers. In addition to the mechanical role of fixing the distance between neighboring porphyrins, the linker provides an electronic role in mediating excited-state energy transfer and/or ground-state hole hopping between the porphyrins. We have employed those types of linkers that provide weak electronic coupling. Weak coupling ensures that the absorption spectra (associated with the first excited singlet state) and electrochemical potentials of the porphyrin building blocks are closely retained upon forming the resulting oligomers. Weak coupling enables rational design based on knowledge of the properties of the component building blocks.[5] Despite the weak coupling, energy transfer in a porphyrin-based light-harvesting array can be exceptionally fast and efficient.[6,7]

Multiporphyrin rods have been synthesized for a variety of applications using methods ranging from the stepwise incorporation of porphyrin building blocks to polymerization of porphyrin monomers. The stepwise methods generally have afforded arrays comprised of eight or fewer porphyrins along the axis of the rod.[1,6–8] The polymerization methods have afforded a variety of architectures, including pendant,[9] cofacial,[10] or backbone oligomers.[11–24] In the backbone oligomers prepared to date, the linkers generally have resulted in large distances of separation (with expected insufficient electronic communication for light-harvesting purposes) between the porphyrins[11–14] or cause the porphyrins to be very tightly coupled electronically.[15–24] Regardless of molecular design and method of synthesis, the use of porphyrins in light-harvesting rods typically presents two problems: poor solubility and limited spectral coverage across the solar spectrum.

One approach to ameliorate the poor solubility of multiporphyrin arrays has been to suppress cofacial aggregation of the porphyrins by incorporating bulky groups at the *meso*-positions of the porphyrins, such as 3,5-di-*tert*-butylphenyl groups[25] or 2,6-disubstituted aryl groups.[26–28] The latter approach has led to the use of mesityl-substituted porphyrins (*e.g.*, *meso*-tetramesitylporphyrin, TMP), which generally have greater solubility than phenyl-substituted porphyrins (*e.g.*, *meso*-tetraphenylporphyrin, TPP). The use of bulky substituents at the non-linking *meso*-positions has led to soluble

---

†Electronic supplementary information (ESI) available: experimental procedures for the synthesis of **2–6**; ^{1}H NMR and LD-MS spectra for all new compounds; ^{1}H NMR, absorption and fluorescence spectra for all oligomers. See http://www.rsc.org/suppdata/jm/b2/b205680a/

DOI: 10.1039/b205680a

multiporphyrin rods in several cases wherein the porphyrins are joined *via* linkers that result in tight electronic communication.[17,23] A related approach incorporated bulky groups on the linker joining the *meso*-positions and afforded soluble multiporphyrin rods.[18] However, in exploratory work leading to the results presented herein, attempted polymerizations of mesityl-substituted porphyrin building blocks (*e.g.*, **1**[29]) resulted in insoluble oligomeric products. We also found that replacement of the methyl groups in porphyrin **1** with ethyl groups (**2**) led to only marginal changes in solubility. Use of very bulky 2,4,6-tris(pentafluorobenzyloxy) groups afforded highly soluble porphyrin building blocks (**3**, **4**), but the resulting oligomers, obtained by polymerization alone or in the presence of capping agent **5** (as a means to modulate the chain length), were quite insoluble and gave intractable films upon removal of solvent (Chart 1). The syntheses of **2**–**5** are described in the electronic supplementary information.†

The limited spectral coverage provided by porphyrins across the solar spectrum is an intrinsic property of the porphyrin chromophore. Porphyrins absorb intensely in the near-UV region but absorb poorly across the remainder of the visible spectrum. By contrast, chlorins and bacteriochlorins both absorb strongly in the blue and red/near-IR regions of the spectrum. The chlorin chromophore (a dihydroporphyrin) and bacteriochlorin chromophore (a tetrahydroporphyrin) form the basis for chlorophyll and bacteriochlorophyll in plant and bacterial photosynthesis, respectively. Porphyrins have been widely employed in light-harvesting studies[8] because of the close structural similarity yet greater synthetic tractability of porphyrins *versus* chlorins or bacteriochlorins. One approach to increase the overall absorption efficiency of porphyrin light-harvesting systems is to employ accessory pigments. A good accessory pigment for porphyrins would absorb light strongly in the trough (430–540 nm) between the porphyrin Soret (B) and Q-bands, transfer energy efficiently to the porphyrin, not engage in electron-transfer quenching with the porphyrin, display good solubility in common organic solvents, and provide compatibility with a modular building block approach.[30,31]

We have investigated the use of perylene-imide dyes as accessory pigments for porphyrins in a number of constructs, including perylene–porphyrin dyads[31–35] and multiperylene–porphyrin arrays.[36] Perylene-imide dyes also have been incorporated in various non-porphyrin dendrimeric architectures.[37] As a general class, perylene-imide dyes meet the criteria for light absorption in the trough between the porphyrin Soret (B) and Q-bands[38] and have the requisite spectral properties for efficient Förster energy transfer (long fluorescence lifetime,[39] high fluorescence quantum yield,[38,40] and respectable overlap

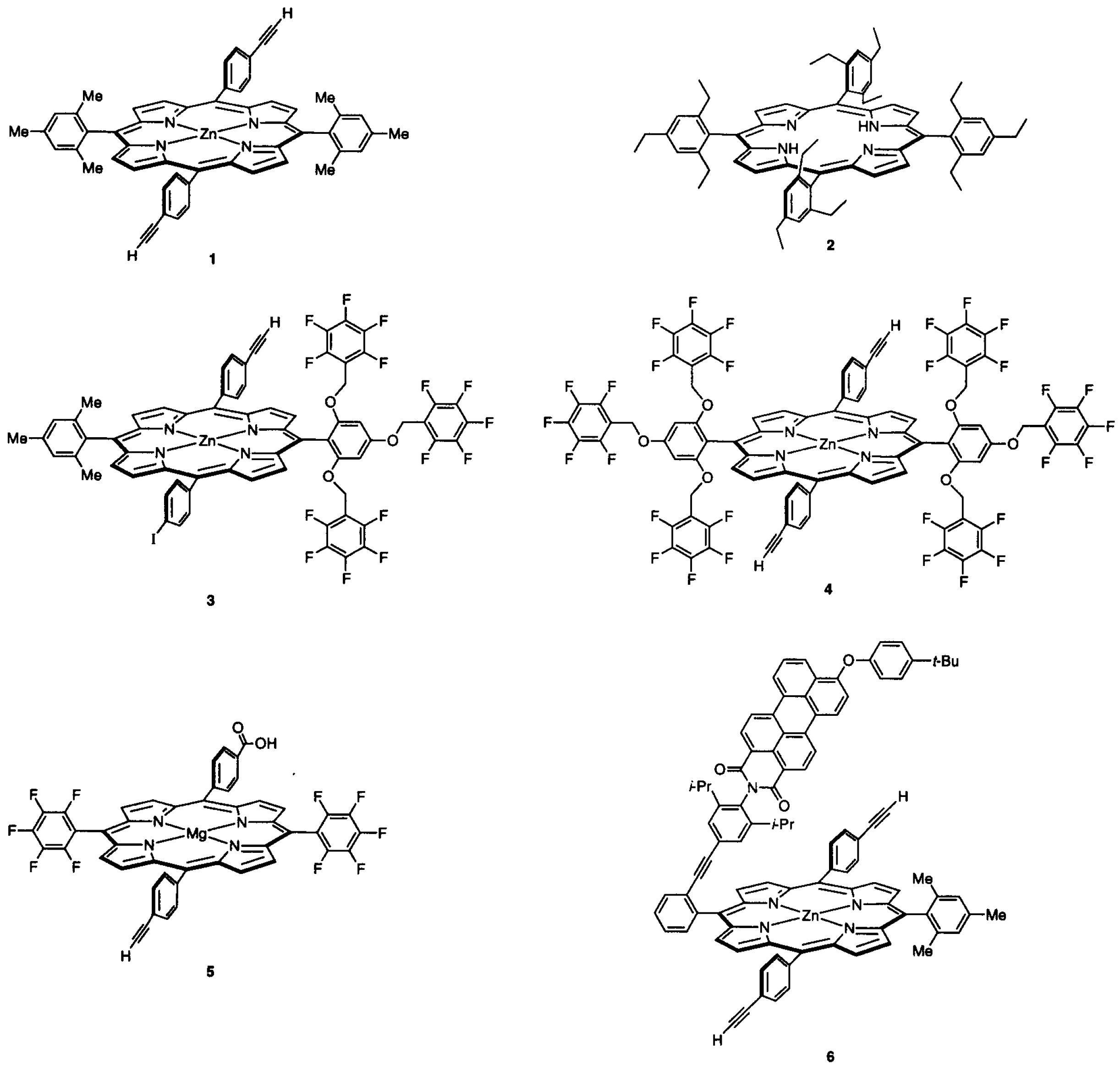


Chart 1

of the fluorescence emission bands with the absorption bands of a zinc porphyrin). However, achieving efficient energy transfer without competing or subsequent electron-transfer quenching processes requires selection of the appropriate composition of the perylene, architecture of the linker, and perylene-linker attachment sites.[31] In addition, the types of substituents on the perylene and the overall perylene–porphyrin architecture affect the solubility of the construct.[31,36]

During our exploratory work aimed at finding suitable perylenes for use with porphyrins, we prepared perylene–porphyrin building block **6** (Chart 1; see electronic supplementary information†). The perylene is a mono-imide derivative, bears a *tert*-butylphenoxy substituent at the 9-position and is attached *via* the *N*-aryl unit to the *o*-position of the *meso*-aryl ring of the porphyrin. The presence of the 9-(4-*tert*-butylphenoxy) substituent and the 2,6-diisopropyl groups served to increase the solubility of the system. The placement of the perylene-monoimide at the *o*-position of the *meso*-phenyl ring of the porphyrin was done with the goal of suppressing cofacial aggregation of the porphyrins. However, when **6** was subjected to Glaser polymerization, an intractable film was obtained.

After much study, we found that perylene-monoimides (rather than perylene-diimides) were viable accessory pigments with porphyrins upon use of a diarylethyne linker joining the *p*-position of the *N*-aryl ring of the perylene and the *meso*-position of the porphyrin.[31,36] For solubility of the perylene, two isopropyl groups are located on the *N*-aryl unit and one or three 4-*tert*-butylphenoxy substituents are positioned on the perylene perimeter. For solubility of the porphyrin, the perylenes are attached at the 2,6- or 3,5-positions of the porphyrin *meso*-aryl group, thereby suppressing cofacial aggregation among neighboring porphyrins in solution. The types of multiperylene–porphyrin light-harvesting architectures (**7**–**11**) that we have prepared are shown in Chart 2.[36] In these constructs, light absorption by the perylene accessory pigment (forming Per*–Por) is followed by rapid excited-state energy transfer ($k_{\text{trans}} > (10\ \text{ps})^{-1}$) from perylene to porphyrin (forming Per–Por*). The properties of the excited porphyrin were examined in non-polar or polar media in order to assess the range of applicability of these types of perylene–porphyrin motifs. In the 3,5-substituted arrays (**8**–**11**), the excited porphyrin exhibits properties resembling those of an isolated porphyrin in non-polar (*e.g.*, toluene) or polar (*e.g.*, benzonitrile) media. In the 2,6-substituted array (**7**), the excited porphyrin exhibits properties resembling those of an isolated porphyrin in toluene but gives a significant diminution of fluorescence emission in benzonitrile. The decline in intensity is indicative of excited-state quenching reactions. Thus, the 3,5-substituted constructs appear suitable for use in a wide range of media whereas the 2,6-substituted constructs are best employed only in non-polar media.

In this paper we present the synthesis and properties of several perylene–porphyrin monomers and the corresponding oligomers. The perylene–porphyrin building blocks are designed based on our studies of perylene–porphyrin dyads and multiperylene–porphyrin arrays. Each building block contains two synthetic handles at the porphyrin 5,15-positions (*trans* architecture); the non-linking 10,20-positions of the porphyrin bear two or four perylene-monoimide dyes attached in a divergent manner at the 3,5-positions of the *meso*-aryl group(s). The building blocks were subjected to Suzuki, Sonogashira, or Glaser coupling reactions in an effort to form oligomers joined by *p*-phenylene (p), 4,4′-diphenylethyne (dpe), or 4,4′-diphenylbutadiyne (dpb) linkers, respectively. Each of these linkers supports efficient energy transfer between porphyrins in dyad architectures.[5,41,42] The absorption, fluorescence, and solubility properties of the oligomers were characterized. This work is a prelude to the use of light-harvesting rods in molecular-based solar cells.

Results and discussion

1 Synthesis of perylene–porphyrin building blocks

The synthesis of a *trans*-AB$_2$C-porphyrin building block required the preparation of a diperylene-dipyrromethane for

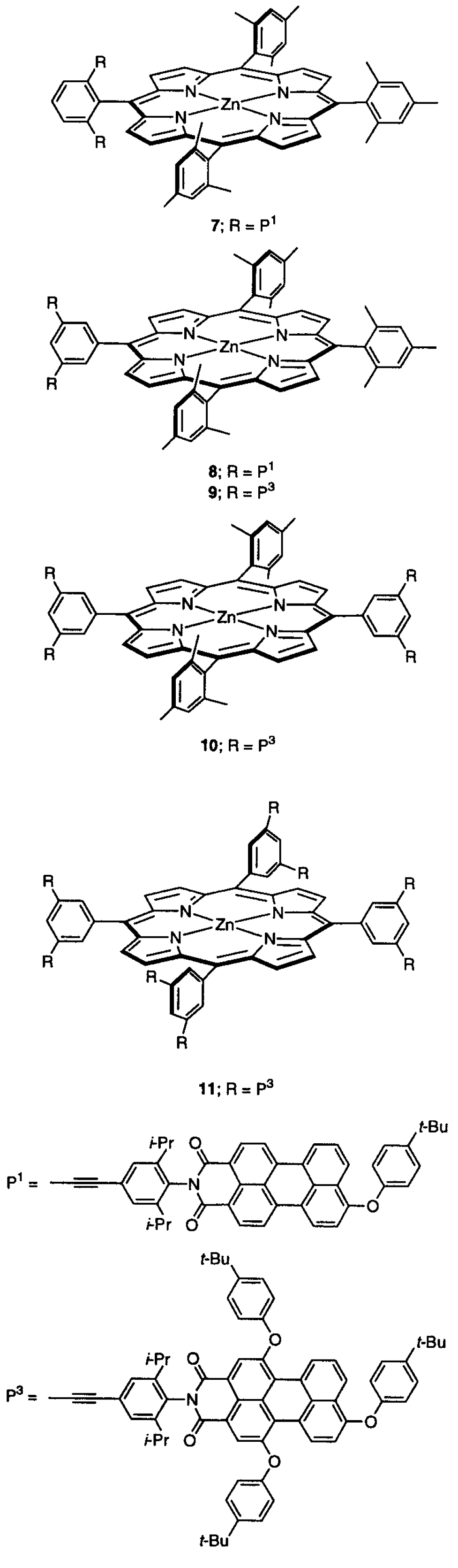
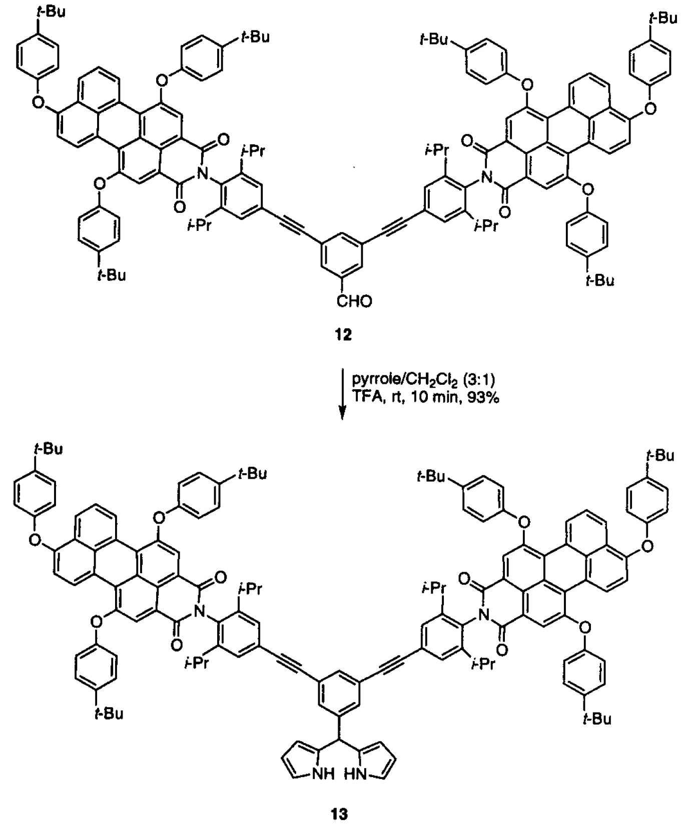


Chart 2



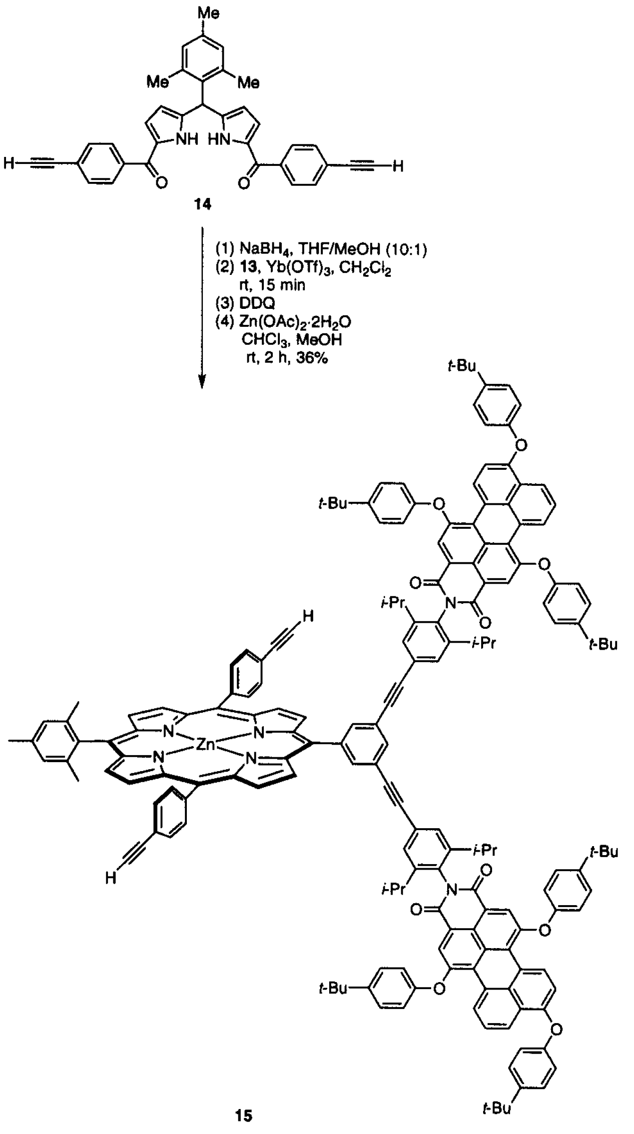
Scheme 1

condensation with a dipyrromethane-dicarbinol. The diperylene-dipyrromethane was prepared by reaction of diperylene-aldehyde **12**[36] with an excess of pyrrole (~400 equivalents) in a modification[43] to the standard literature procedure.[44] A small amount of methylene chloride was added to achieve full solvation of the diperylene-aldehyde. Addition of TFA and reaction for 10 min at room temperature afforded diperylene-dipyrromethane **13** in 93% yield after chromatographic workup (Scheme 1).

Preparation of the *trans*-AB_2C-porphyrin is shown in Scheme 2. Reduction of diacyldipyrromethane **14**[43] using excess $NaBH_4$ in THF–MeOH (10 : 1) afforded the corresponding dipyrromethane-dicarbinol. We performed the dipyrromethane + dipyrromethane-dicarbinol condensation using new catalysis conditions that employ a Lewis acid [$InCl_3$, $Sc(OTf)_3$, $Yb(OTf)_3$, or $Dy(OTf)_3$] in CH_2Cl_2 at room temperature.[45] Compared to TFA catalysis (30 mM in CH_3CN at room temperature),[46] these conditions can provide increased yields of porphyrin and a simplified purification procedure. The dicarbinol was then immediately condensed with diperylene-dipyrromethane **13** using $Yb(OTf)_3$ (3.2 mM) in CH_2Cl_2. Oxidation with DDQ followed by zinc metalation afforded perylene–porphyrin building block **15** in 36% yield. Perylene–porphyrin **15** bears two ethynylphenyl synthetic handles in a *trans* architecture, thereby enabling a Glaser reaction to produce perylene–porphyrin oligomers.

An ABCD-porphyrin bearing two perylenes was prepared as shown in Scheme 3. Diacyldipyrromethane **16**[46] was treated with TBAF on silica (1.0–1.5 mmol F^-/g resin) to afford diacyldipyrromethane **17** in 97% yield. Reduction of **17** with excess $NaBH_4$ in THF–MeOH (10 : 1) afforded the dipyrromethane-dicarbinol as a foam-like solid. Condensation of the dicarbinol with diperylene-dipyrromethane **13** under identical conditions as described for **15** [$Yb(OTf)_3$ (3.2 mM), CH_2Cl_2], followed by oxidation with DDQ and metalation with $Zn(OAc)_2 \cdot 2H_2O$ furnished porphyrin **18** in 30% yield. We have also prepared **18** in 12% yield directly from the dicarbinol of the TMS-protected diacyldipyrromethane **16**. In this case an additional step, consisting of TMS deprotection of the zinc porphyrin was needed to furnish the porphyrin **18**. The lower overall yield from **16** as compared with that from **17** is due to the low yield of the TMS cleavage from porphyrin **18** and not to the porphyrin-forming reaction. The resulting perylene–porphyrin building block bears one ethynylphenyl and one iodophenyl functional group in a *trans* architecture, thereby enabling a Sonogashira reaction to prepare a linear perylene–porphyrin oligomer.

A building block bearing a perylene at each of the 3,5-positions of the two non-linking *meso*-aryl rings of the *trans*-porphyrin was also prepared. Our initial synthetic approach called for the monoacylation of diperylene-dipyrromethane **13** with *S*-2-pyridyl 4-ethynylbenzothioate (**19**)[47] to yield diperylene-monoacyldipyrromethane **20**. Reduction of **20** with $NaBH_4$ followed by self-condensation was expected to yield the *trans*-A_2B_2-porphyrin. However, treatment of **13** with EtMgBr followed by cooling to −78 °C and reaction with **19** afforded starting material **13** rather than the desired diperylene-monoacyldipyrromethane **20** after workup (Scheme 4). Accordingly, the target perylene–porphyrin building block was prepared as shown in Scheme 5. Condensation of dipyrromethane **13** and aldehyde **21**[48] using TFA in CH_2Cl_2 at room temperature for 1 h followed by oxidation with DDQ afforded the crude porphyrin mixture. These are the conditions typically employed for reaction of a sterically hindered dipyrromethane with an aldehyde.[49] Although sterically unhindered dipyrromethanes (*i.e.*, no *o*-substituents on the *meso*-phenyl ring) typically undergo acidolysis under these conditions,[49] analysis of the crude reaction mixture by LD-MS showed no detectable formation of rearranged products derived from acidolysis (*i.e.*, scrambling). The crude porphyrin was metalated with $Zn(OAc)_2 \cdot 2H_2O$ to furnish the *trans*-A_2B_2-porphyrin building block **22** in 23% yield. This building block bears two ethynylphenyl



Scheme 2

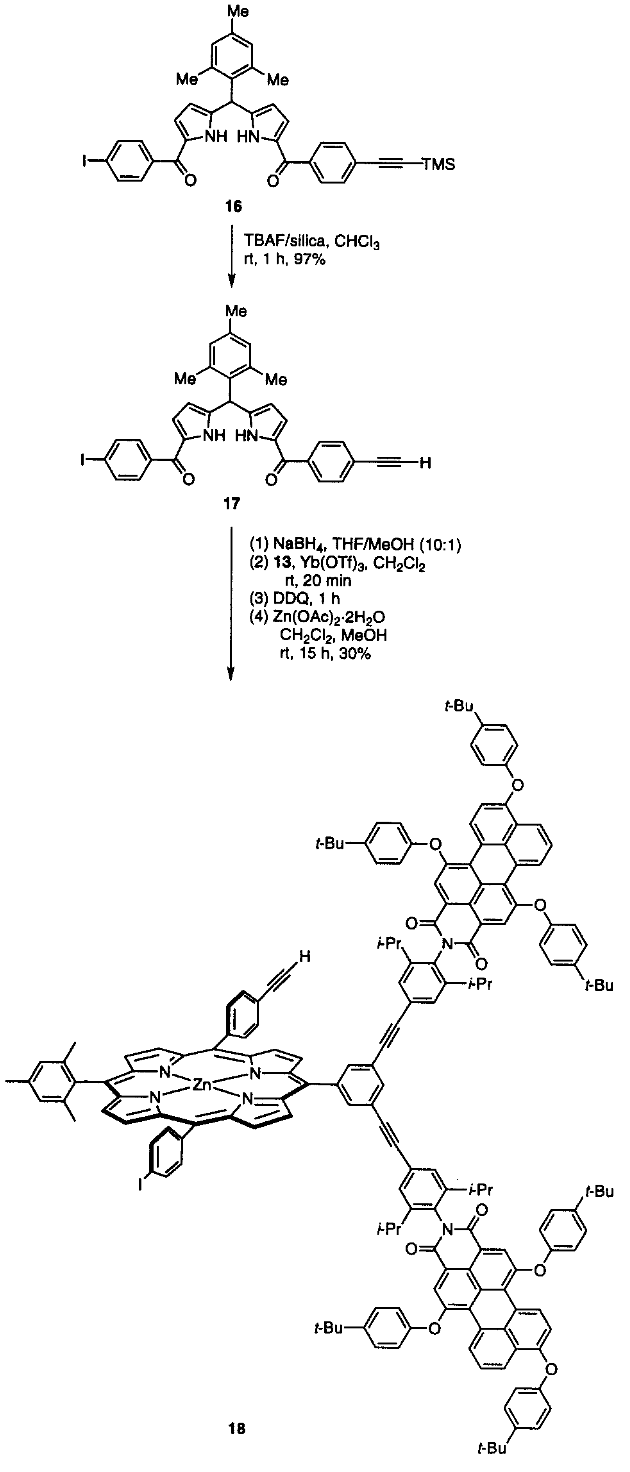
synthetic handles that can be polymerized using the Glaser reaction.

A dibromo-porphyrin building block for use in a Suzuki polymerization was synthesized as shown in Scheme 6. Condensation of diperylene-aldehyde **12** with dipyrromethane (**23**) under TFA catalysis followed by oxidation with DDQ afforded the crude porphyrin. Metalation using Zn(OAc)$_2$·2H$_2$O in CHCl$_3$–MeOH afforded porphyrin **24** in 43% yield. The two free *meso*-positions of porphyrin **24** were subsequently brominated using NBS in CHCl$_3$–pyridine,[50] affording dibromoporphyrin **25** in 72% yield. Bromination occurred regiospecifically at the two *meso*-positions; bromination was not observed at the β-positions of the porphyrin, at the perimeter of the perylene, or at the aryloxy rings attached to the perylene.

The synthesis of the other monomeric component for the Suzuki polymerization is shown in Scheme 7. Commercially available 1,4-bis(dihydroxyboryl)benzene was treated with pinacol in anhydrous DMF at room temperature for 12 h, affording compound **26** in 93% yield.

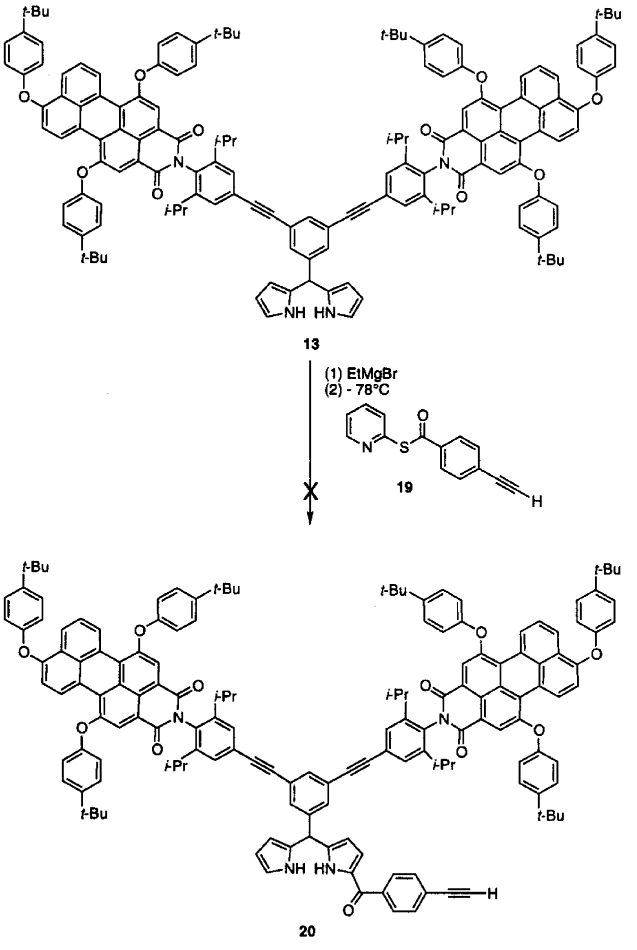
2 Polymerization of perylene–porphyrin building blocks

Our objective in gaining access to light-harvesting rods is to employ the rods as the active material in a molecular-based solar cell. The general design of such a cell incorporates the rods in a sandwich architecture between two planar semiconductive



Scheme 3

or conductive substrates, where the rods are essentially normal to the substrates and at least one of the substrates is transparent. The rods provide four functions: absorption of light, transfer of excited-state energy along the length of the rod, injection of an electron from the terminal unit in the rod into the semiconductor, and migration of the resultant hole toward the opposite end of the rod.[1] To absorb a significant fraction of the incident light in such a design, rods composed of ~20 porphyrins with appended perylenes appear to be suitable. A first step toward such a molecular-based solar cell requires the ability to convert monomeric photoactive building blocks into soluble rod-like oligomers that exhibit appropriate light-harvesting properties. Additional issues that are germane to the construction of such a cell, such as the derivatization of

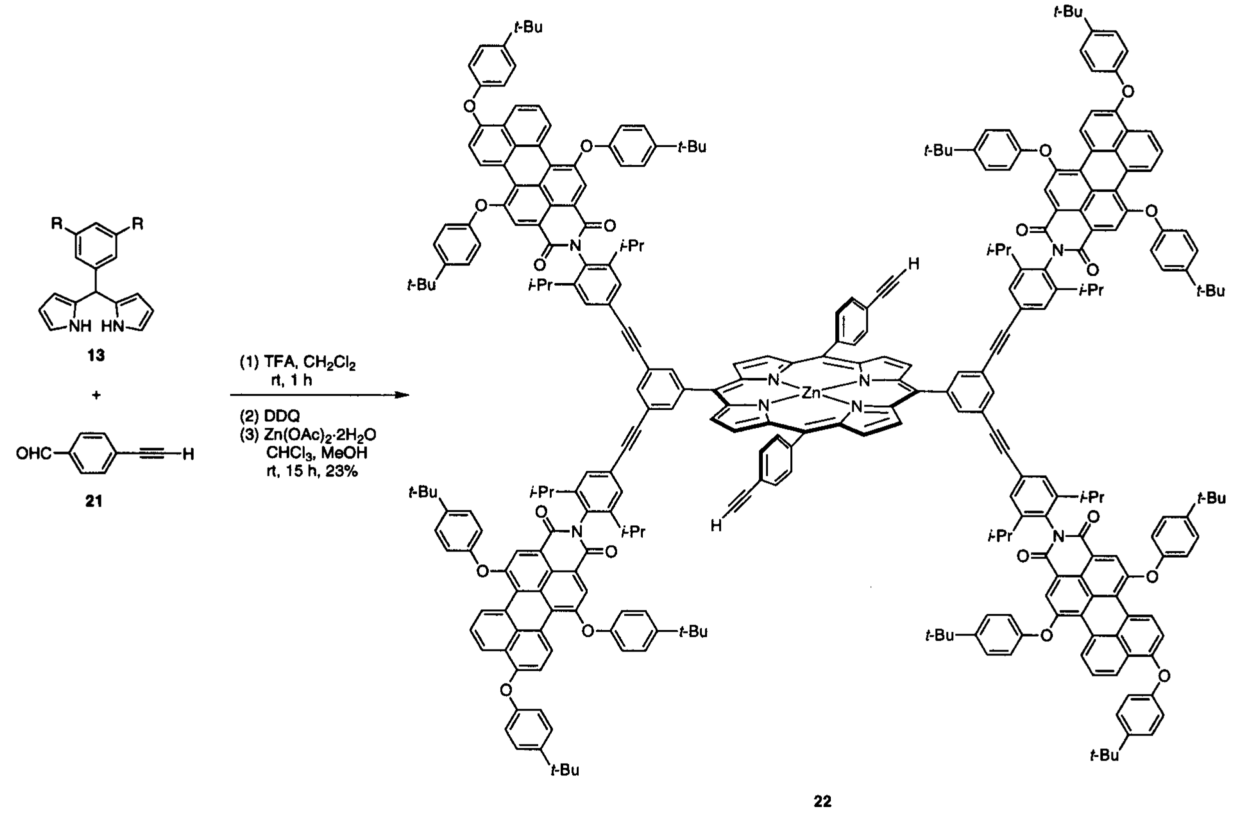


Scheme 4

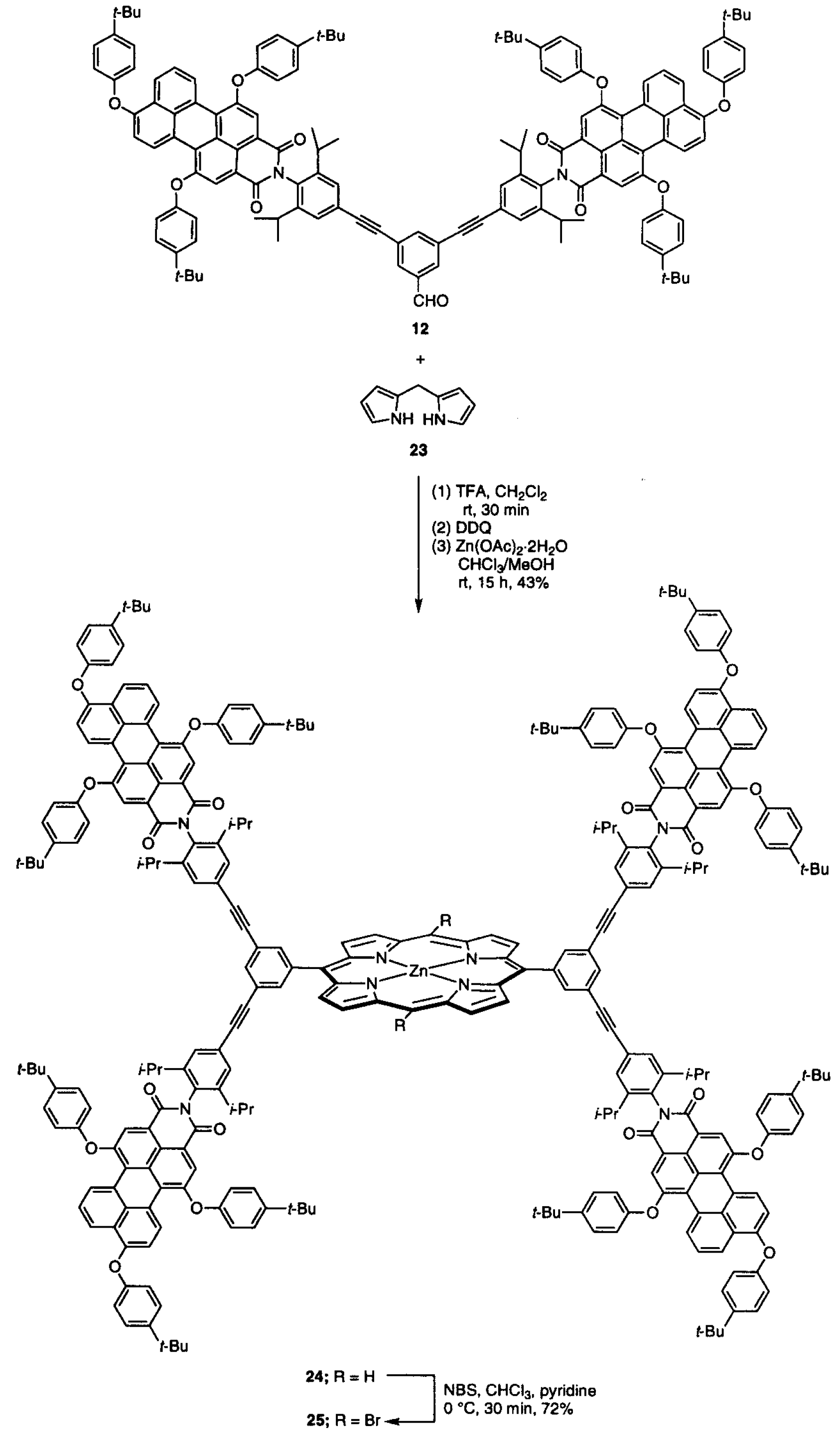
the rods with appropriate surface attachment groups, can only be addressed upon gaining robust access to soluble light-harvesting rods.

Our goals in the work reported herein were to investigate the utility of the perylene–porphyrin building blocks in several different polymerization schemes, including the Glaser, Sonogashira, and Suzuki reactions. Both the Glaser[16,17] and Sonogashira[18] reactions have been used previously to prepare multiporphyrin rods. The issues we sought to address included the stability of the building blocks to the conditions employed in the coupling reactions, the size of the oligomers that can be readily produced, the solubility of the oligomers, and the absorption and fluorescence properties of the oligomers. This work provides the foundation for the preparation of perylene–porphyrin oligomers bearing surface attachment units for use in solar cells. A summary of the polymerizations that were carried out is shown in Table 1.

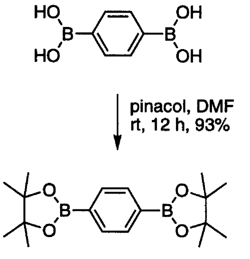
Glaser polymerizations. Glaser reactions were performed with the diethynyl porphyrins **6**, **15**, and **22** (Scheme 8). In each case, the polymerization was performed at room temperature in the presence of air with the diethynyl porphyrin at a concentration of 2.5 mM. The conditions for the Glaser polymerization entailed a Pd-mediated method using Pd($(PPh_3)_2Cl_2$, CuI, and I_2 in toluene containing *N,N*-diisopropylethylamine.[51] We employed these conditions directly for **6** and **15**, but omitted the I_2 in the reaction of **22**. We found that the reaction proceeded well in the absence of I_2, at least with the dilute solutions and small quantities employed in these experiments. In each case, the course of the reaction was followed by analytical size exclusion chromatography (SEC). The results for the reaction of **22** are shown in Fig. 1. Within 20 min of reaction, oligomers of significant length were formed. Analytical SEC showed resolution of discrete oligomers up to the octamer stage, though the SEC trace suggested the presence of oligomers of substantially greater length. After 40 min, the analytical SEC showed only a small amount of monomer and



Scheme 5



Scheme 6



Scheme 7

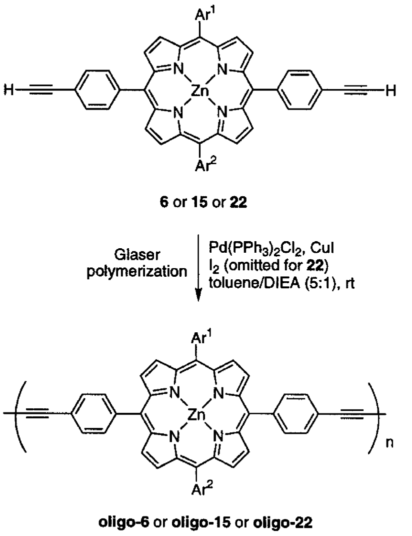
small oligomers (2–5 units) with the majority of the peak containing a distribution of larger oligomeric materials. The reaction was stopped after 1 h. Similar results were obtained for the polymerization of **6** and **15** (not shown).

In each case, workup of the crude reaction mixture entailed concentration to near dryness followed by addition of THF. In the case of **6**, the product did not dissolve in THF but instead formed a dark film on the walls of the flask. The insolubility of **oligo-6** precluded further processing and characterization. However, the products of the polymerization of **15** and **22** did dissolve in THF. **Oligo-15** was purified by preparative SEC to remove reagents and low molecular weight species, with the oligomeric material eluting as a tight red band that was isolated and concentrated to dryness. The resulting oligomer was twice

Table 1 Characteristics of perylene–porphyrin building blocks and resulting oligomers

Entry	Number of perylenes	Number of ArO- groups	Site of attachment	Monomer	Polymerization type	Linker
1	1	1	2-	**6**[a]	Glaser	4,4′-Diphenylbutadiyne
2	2	3	3,5-	**15**	Glaser	4,4′-Diphenylbutadiyne
3	2	3	3,5	**18**	Sonogashira	4,4′-Diphenylethyne
4	4	3	3,5	**22**	Glaser	4,4′-Diphenylbutadiyne
5	4	3	3,5	**25**[b]	Suzuki	1,4-Phenylene

[a] The product was insoluble and not characterized. [b] Only very short oligomers were formed.



Scheme 8

triturated with methanol, centrifuged, and the supernatant was decanted. The same process was then performed with hexanes, affording a purple powder. **Oligo-22** was purified by column chromatography (silica) to remove coupling reagents, then concentrated to dryness and triturated with methanol, affording a purple powder.

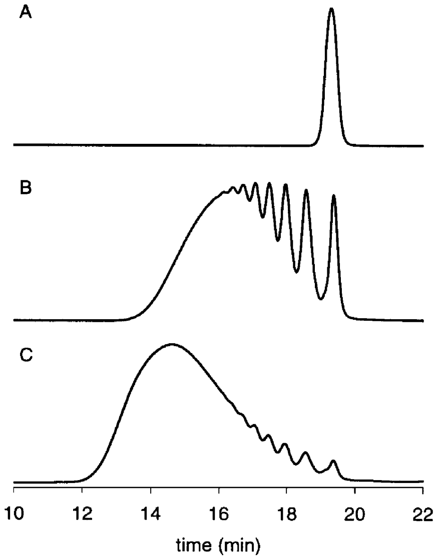


Fig. 1 Analytical SEC traces (a 10^4 Å column and 10^3 Å column in series) of the Glaser polymerization of **22** affording the diphenylbutadiynyl-linked product (**oligo-22**). Each porphyrin bears four perylenes. (A) Starting perylene–porphyrin **22**. (B) Reaction mixture after 20 min. (C) Final reaction mixture after 40 min. The chromatograms are normalized (uncorrected absorption data).

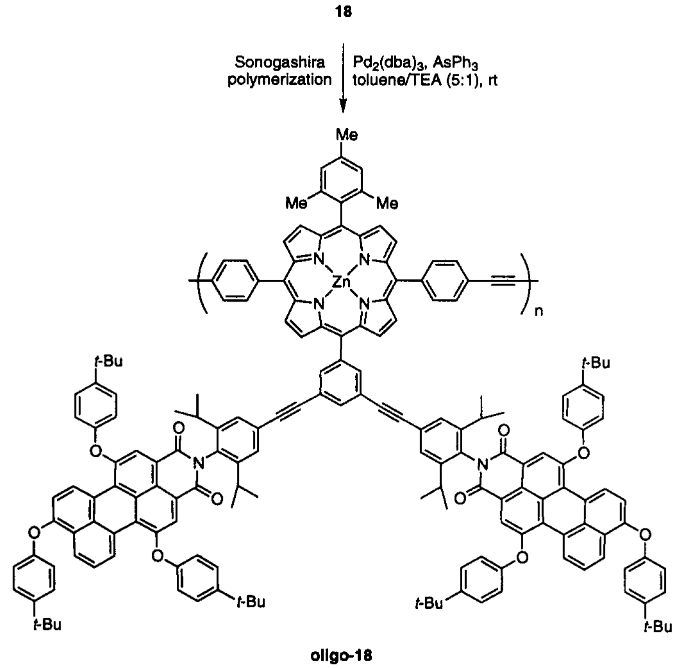
Sonogashira polymerization. A Sonogashira reaction was carried out using building block **18** as shown in Scheme 9. The conditions for the reaction were drawn from those developed for use with ethynyl- and iodo-substituted porphyrins in dilute solution.[52] The conditions are copper-free, anaerobic (Schlenk line), and employ $Pd_2(dba)_3$ (15 mol%) and $AsPh_3$ (120 mol%) in toluene–triethylamine (5 : 1) at room temperature with the porphyrin at a concentration of 2.5 mM. These conditions are gentle and minimize homo-coupling. The analytical SEC traces showing the progress of the reaction are displayed in Fig. 2. After 2 h, analytical SEC showed monomer, dimer, and traces of trimer through to pentamer. After 22 h, the analytical SEC revealed a distribution of oligomers. Resolution of the discrete oligomers was observed up to the 11-mer, though the SEC trace suggested the presence of a distribution of oligomers of substantially greater length. The crude product was purified in the same manner as described for **oligo-15**, yielding **oligo-18**.

Suzuki polymerization. The Suzuki reaction has been applied by Chan[53] and others[54–56] to attach diverse groups to porphyrins and to prepare porphyrin dyads joined by elaborate linkers. By contrast, relatively few examples have been reported for preparing *p*-phenylene linked porphyrin arrays, and these pertain only to dimers[55,56] and trimers.[56] Regardless of the synthetic target, all applications of the Suzuki reaction with porphyrins have employed substantially more forcing conditions than those used for the Sonogashira or Glaser reactions.

The Suzuki reaction of **25** and **26** is shown in Scheme 10. We carried out the reaction of **25** and **26** under the conditions employed previously for Suzuki couplings yielding *p*-phenylene linked porphyrin dimers and trimers.[56] The reaction conditions employ $Pd(PPh_3)_4$ and K_2CO_3 (8 equiv.) in toluene–DMF (2 : 1) at 90 °C. Under these reaction conditions, only a small amount of short oligomers (2–5 units) was detected by analytical SEC, even after prolonged reaction times (48 h). After several hours, analytical SEC showed the presence of additional peaks due to species of apparently smaller size than the starting monomer. Absorption spectral analysis showed some of the peaks to have broad perylene bands with no porphyrin absorption, indicating some decomposition of the perylene–porphyrin monomer under these reaction conditions. Therefore, further Suzuki polymerizations were not attempted. It is noteworthy that linear *p*-phenylene-linked rods containing up to nine porphyrins have been prepared *via* successive condensations,[57] a route complementary to that of the Suzuki polymerization.

3 Physical properties of the oligomers

The solubilities of **oligo-6**, **oligo-15**, **oligo-18**, and **oligo-22** were assessed in four typical organic solvents spanning a range of polarity, including toluene, tetrahydrofuran, chloroform, and benzonitrile. Rather than attempting to determine the maximum solubility, we sought to assess an operational solubility for routine handling, which includes chromatography, characterization, and processing. Thus, we elected to determine whether the dry oligomeric material would dissolve at a concentration of 2.5 mM within one minute upon treatment



Scheme 9

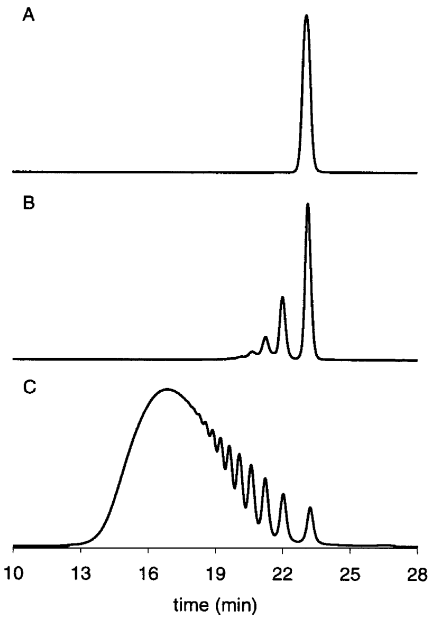


Fig. 2 Analytical SEC traces (a 10^4 Å column and a 10^3 Å column in series) of the Sonogashira polymerization of **18** affording the diphenylethynyl-linked product (**oligo-18**). Each porphyrin bears two perylenes. (A) Starting perylene–porphyrin **18**. (B) Reaction mixture after 2 h. (C) Final reaction mixture after 22 h. The chromatograms are normalized (uncorrected absorption data).

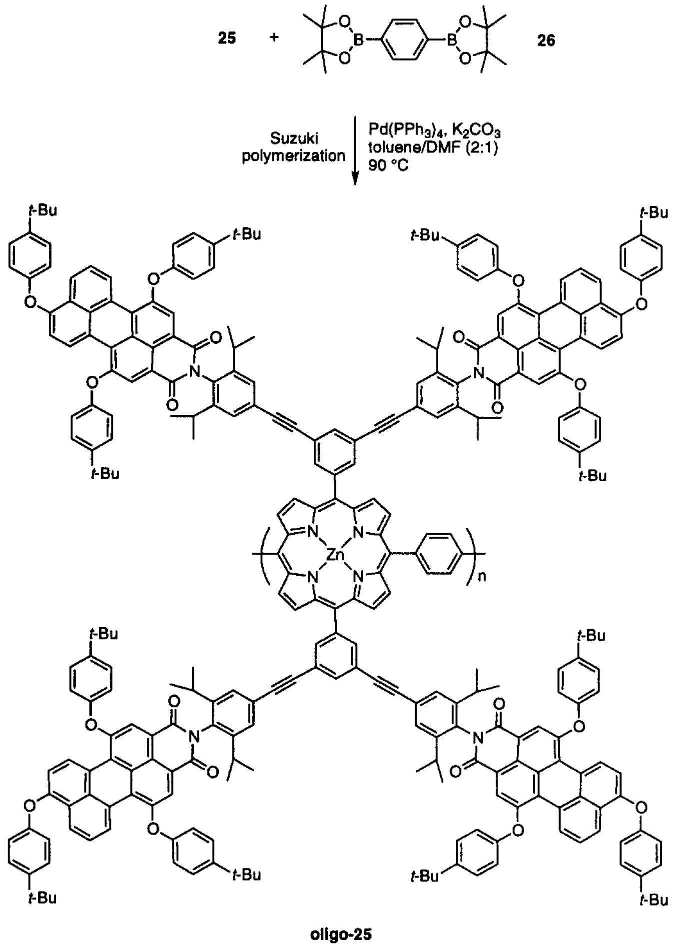
with a given solvent at room temperature. The resulting samples were examined visually and classified as completely soluble, partially soluble, or insoluble. The results of this survey are shown in Table 2. **Oligo-15** and **oligo-22** each were soluble (at 2.5 mM) in toluene, THF, and chloroform, but only partially soluble in benzonitrile. **Oligo-18** was partially soluble in all four solvents examined. The higher solubility of **oligo-15** compared to **oligo-18** (both have two perylenes per porphyrin) is attributed to the different linkers (dpb *vs.* dpe, respectively), given that the dpb linker is longer and provides additional bending[58] compared with the dpe linker. **Oligo-22** was the most soluble of the three samples, which is due to the presence of four perylenes per porphyrin and to the dpb linker.

Each oligomer sample was subjected to analysis by laser-desorption mass spectrometry (LD-MS) and matrix-assisted laser-desorption mass spectrometry (MALDI-MS). For each sample, both the LD-MS and MALDI-MS were uninformative, as a distribution of molecule ion peaks stemming from the distribution of oligomers was not observed. In some cases, a series of weak peaks could be seen but the poor signal-to-noise and lack of resolution prevented informative analysis.

Proton NMR spectra were collected for **oligo-15**, **oligo-18**, and **oligo-22** (see electronic supplementary information†). The ^{1}H NMR spectra of these oligomer samples resembled those of their respective monomers (as expected from weakly coupled systems), though many of the resonances from the oligomeric samples were broadened and lacked resolution.

The absorption spectra and fluorescence spectra of these oligomers were also collected. All three samples displayed a splitting and broadening of the Soret band compared with the spectra of the respective monomers. The absorption spectrum of **oligo-18** shown in Fig. 3 is representative. While the Q-band region of porphyrins is typically unaffected upon incorporation into arrays joined by 1,4-diphenylbutadiyne,[42] 1,4-diphenylethyne,[5] or 1,4-phenylene linkers,[41] the strong absorption of the perylene dye in each case prevented detailed examination of this Q-band region in these oligomers. Regardless, the magnitude of the changes in the Soret band, the lack of significant changes in the absorption of the perylene, and emission spectra qualitatively unchanged from those of the corresponding component parts collectively indicate that the electronic interactions in the oligomers are relatively weak.

Two types of static fluorescence spectroscopic measurements were made on the oligomers: (1) examination of the fluorescence yield of the porphyrin to assess whether the presence of the perylenes causes quenching of the porphyrin, and (2) examination of the fluorescence emission spectrum upon illumination of the perylene to assess the extent of energy transfer from the perylene to the porphyrin. Thus, **oligo-18** (in toluene at room temperature) was illuminated at 423 nm, where the absorption of the zinc porphyrin is dominant (for example, at 423 nm the standard zinc porphyrin ZnTPP absorbs 160 times that of the corresponding benchmark perylene-monoimide



Scheme 10

Table 2 Solubility of oligomers produced from perylene–porphyrin building blocks[a]

Solvent	Oligo-6	Oligo-15	Oligo-18	Oligo-22
Toluene	−	+	±	+
THF	−	+	±	+
$CHCl_3$	−	+	±	+
Benzonitrile	−	±	±	±

[a] A known volume of solvent was added to a known mass of oligomer. Full solvation resulted in a porphyrin concentration of 2.5 mM. + = soluble at 2.5 mM; ± = partially soluble (less than 2.5 mM); − = not soluble.

dye (**27**)[31] (Chart 3)). The resulting emission occurred nearly exclusively from the zinc porphyrin with the fluorescence quantum yield comparable to that of ZnTPP ($\Phi_f = 0.033$).[59] Illumination of **oligo-18** at 490 nm, where the perylene absorbs preferentially (the absorption of perylene **27** is 17 times that of ZnTPP at 490 nm), results in emission predominantly from the porphyrin with a small amount of emission from the perylene (Fig. 3 inset). The fluorescence emission from the perylene was diminished by ~80-fold compared with that of the benchmark perylene **27**. The fluorescence quantum yield of **27** is nearly quantitative. The fluorescence properties of **oligo-15** and **oligo-22** were comparable to those of **oligo-18**. Taken together, these data indicate that energy transfer from the perylene to the porphyrin occurs efficiently and the porphyrin excited state is relatively unaffected by the presence of the multiple perylenes. The same behavior was exhibited by the related, non-oligomeric arrays **9** and **10**.[36] Exciton migration along the backbone of the oligomers is expected to be rapid, a process not possible in arrays **9** or **10**, but one that can lead to extensive quenching if one or more quenching sites are present somewhere along the rod.[60] However, the data in hand indicate the presence of the expected photochemical processes and the absence of new deleterious processes. Additional spectroscopic measurements, including time-resolved spectroscopy, are required to quantitate the rates and efficiencies of the energy-transfer processes in the multiperylene–porphyrin oligomers.

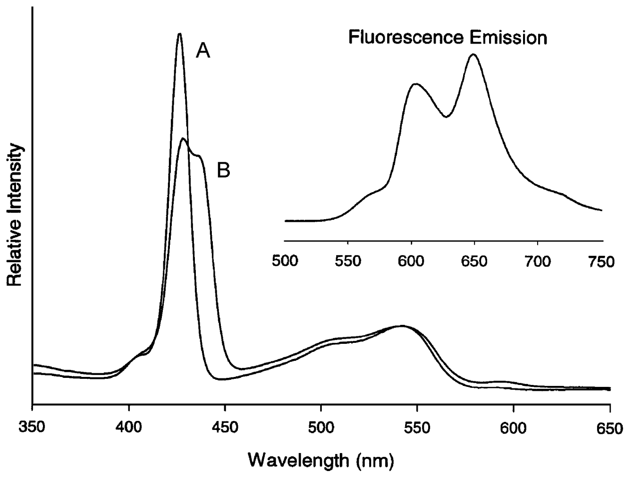
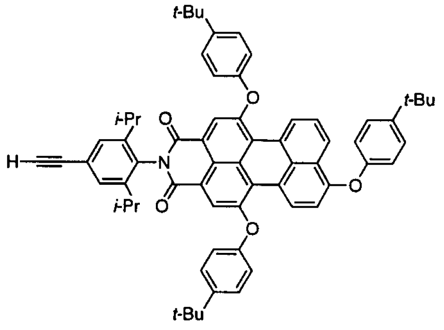


Fig. 3 Absorption spectra for **18** (A) and **oligo-18** (B) in toluene at room temperature (normalized at 538 nm, the peak of the absorption due to perylene and the porphyrin Q band). Inset: fluorescence emission spectrum for **oligo-18** in toluene at room temperature (λ_{ex} = 490 nm).



27

Chart 3

Conclusion

We have prepared new perylene–porphyrin building blocks bearing ethynylphenyl, iodophenyl, and/or bromo substituents at the 5,15-positions of the porphyrin macrocycle. The perylenes provide enhanced spectral coverage and increased solubility compared with use of porphyrins alone. These building blocks serve as monomers for use in the Glaser, Sonogashira, and Suzuki reactions. The Glaser polymerization is generally rapid, affording sizeable oligomers at room temperature in a few minutes. The Sonogashira polymerization also produced sizeable oligomers, but required longer reaction times ($\sim$24 h) at room temperature. Attempts to prepare oligomers using the Suzuki reaction were unsuccessful. The oligomers examined exhibited sufficient solubility in common organic solvents for routine handling. The spectral and energy-transfer properties displayed by these oligomers bode well for their use as components in molecular-based solar cells.

Experimental

General

^{1}H (300 or 400 MHz) and ^{13}C (75 MHz) NMR spectra were recorded in $CDCl_3$ unless noted otherwise. Mass spectra of porphyrins and perylene–porphyrin arrays were obtained by high-resolution fast atom bombardment (FAB) and/or by laser desorption mass spectrometry (LD-MS).[61] Absorption and emission spectra were collected in toluene at room temperature unless noted otherwise. Elemental analyses were performed by Atlantic Microlab, Inc. Melting points are uncorrected. Silica gel (Baker 40 µm average particle size) and alumina (Fisher, 80–200 mesh) were used for column chromatography. Preparative SEC was performed using BioRad Bio-Beads SX-1 (200–400 mesh) beads. Analytical SEC was performed using an HP 1100 Series Liquid Chromatograph [column size = a 10^4 Å column and 10^3 Å column in series); flow rate = 0.800 mL min^{-1}; solvent = THF; quantification at 420 and 510 nm; reference at 670 nm; oven temperature 25 °C].[6] Toluene and triethylamine were freshly distilled from CaH_2 and sparged with argon prior to use. Chloroform contained 0.8% ethanol as a stabilizer. All reagents were purchased from Aldrich and used as received.

Palladium-mediated coupling reactions

All Sonogashira coupling reactions were performed using a Schlenk line. The conditions for Sonogashira reactions with porphyrins use tris(dibenzylideneacetone)dipalladium(0) [$Pd_2(dba)_3$] and $AsPh_3$ in the absence of any copper reagents. Palladium insertion and transmetalation have not been observed with these conditions.[52] All Glaser coupling reactions were performed in air using $Pd(PPh_3)_2Cl_2$, CuI, and I_2 (except for **22**).[51] For both reactions, the concentration of the building blocks was 2.5 mM.

Non-commercial compounds

Porphyrin **1**,[29] dipyrromethanes **14**,[43] **16**,[46] and **23**,[49] aldehydes **12**[36] and **21**,[48] benzothioate **19**,[47] and perylene **27**[31] were prepared as described in the literature.

Solubility experiments

The oligomers were assessed for solubility in a given solvent at room temperature. A known quantity of a dry powder (*e.g.*, 2.0 mg) was weighed into a vial. A known volume of solvent (*e.g.*, 200 µL) was added to achieve a target concentration per porphyrin of 2.5 mM. After one minute with occasional manual swirling, the mixture was assessed visually for homogeneity. In this manner, operational solubility at a workable concentration could be established.

Polymerization experiments

Polymerization of the porphyrins was achieved by Pd-mediated coupling under Glaser, Sonogashira, or Suzuki conditions. Reactions were carried out using 2–7 µmol of porphyrin monomer. For cases where less than 2.0 mg of a coupling reagent was needed, stock solutions were prepared to deliver accurate amounts to the reaction. For example, CuI was dissolved in diisopropylethylamine (DIEA) to make a 3.8 mM stock solution, I_2 was dissolved in toluene to make a 45 mM stock solution, and $Pd(PPh_3)_2Cl_2$ was dissolved in toluene to make a 7.1 mM stock solution. All reactions were monitored by analytical SEC.

5-[3,5-Bis(2-{4-[1,6,9-tris(4-*tert*-butylphenoxy)perylene-3,4-dicarboximido]-3,5-diisopropylphenyl}ethynyl)phenyl]dipyrromethane (13)

Following a modification[43] to a standard procedure,[44] a solution of **12** (623 mg, 311 µmol) in pyrrole (9.0 mL, 0.13 mol) and CH_2Cl_2 (3.0 mL) was treated with TFA (2.4 µL, 31 µmol). The mixture was stirred at room temperature for 10 min. TEA and CH_2Cl_2 were added and the mixture was washed with brine. The organic layer was dried (Na_2SO_4), chromatographed [silica, $CH_2Cl_2 \rightarrow CH_2Cl_2$–ethyl acetate (99.5 : 0.5)], and triturated with hexanes to afford a magenta solid (614 mg, 93%): ^{1}H NMR δ 1.15 (d, J = 6.6 Hz, 24H), 1.32 (s, 18H), 1.34 (m, 36H), 2.67–2.76 (m, 4H), 5.49 (s, 1H), 5.98 (m, 2H), 6.18–6.20 (m, 2H), 6.73 (m, 2H), 6.88 (d, J = 8.8 Hz, 2H), 7.02 (d, J = 8.8 Hz, 4H), 7.08 (d, J = 8.8 Hz, 4H), 7.09 (d, J = 8.8 Hz, 4H), 7.37 (d, J = 8.8 Hz, 4H), 7.40–7.45 (m, 14H), 7.59–7.64 (m, 2H), 7.70 (s, 1H), 8.01 (br s, 2H), 8.31 (s, 2H), 8.34 (s, 2H), 8.47 (d, J = 8.8 Hz, 2H), 9.23 (d, J = 8.8 Hz, 2H), 9.43 (d, J = 8.1 Hz, 2H); ^{13}C NMR δ 24.1, 29.3, 29.9, 31.7, 34.6, 43.9, 88.5, 90.8, 107.8, 108.8, 111.8, 117.8, 118.3, 118.5, 120.0, 120.5, 121.4, 122.3, 123.7, 124.0, 124.2, 124.5, 124.8, 125.1, 126.0, 126.8, 127.1, 127.3, 127.4, 127.7, 127.9, 128.2, 130.0, 130.1, 130.9, 131.5, 131.6, 131.8, 133.7, 142.9, 146.4, 147.1, 147.3, 147.8, 152.7, 153.5, 153.6, 156.2, 163.4; MALDI-MS (dithranol) obsd 2122.09 [M$^+$], 2056.96 [(M − pyrrole)$^+$], 1974.11 [(M − 4-*t*-BuPhO)$^+$], calcd 2118.67 ($C_{147}H_{136}N_4O_{10}$); λ_{abs} 536 nm; λ_{em} (λ_{ex} = 540 nm) 575, 623(sh) nm.

Zn(II)-5-[3,5-Bis(2-{4-[1,6,9-tris(4-*tert*-butylphenoxy)perylene-3,4-dicarboximido]-3,5-diisopropylphenyl}ethynyl)phenyl]-15-mesityl-10,20-bis(4-ethynylphenyl)porphyrin (15)

Following a standard procedure[46] with improved acid catalysis conditions,[45] a sample of **14** (46.0 mg, 99.1 µmol) was reduced with $NaBH_4$ (74.0 mg, 1.98 mmol) in THF–methanol [5.0 mL (10 : 1)]. The resulting dipyrromethane-dicarbinol was condensed with **13** (210 mg, 99.1 µmol) in CH_2Cl_2 (40 mL) containing $Yb(OTf)_3$ (79.0 mg, 128 μmol, 3.2 mM) for 15 min. DDQ (68.0 mg, 300 μmol) was added and the mixture was stirred at room temperature for 1 h. The mixture was neutralized with TEA then filtered through a silica column [CH_2Cl_2–hexanes (2 : 1)]. The residue was treated with $Zn(OAc)_2{\cdot}2H_2O$ (110 mg, 500 μmol) in $CHCl_3$ (20 mL) and methanol (5.0 mL) at room temperature for 2 h. The mixture was washed with water. The organic phase was dried (Na_2SO_4) and chromatographed [silica, CH_2Cl_2–hexanes (2 : 1)]. The product was concentrated, then triturated with hexanes affording a red solid (95.5 mg, 36%): ^1H NMR δ 1.13 (d, J = 6.6 Hz, 24H), 1.30 (s, 18H), 1.33 (s, 18H), 1.34 (s, 18H), 1.84 (s, 6H), 2.64–2.74 (m, 7H), 3.31 (s, 2H), 6.89 (d, J = 8.8 Hz, 2H), 7.01 (d, J = 8.8 Hz, 4H), 7.06 (d, J = 8.8 Hz, 4H), 7.08 (d, J = 8.8 Hz, 4H), 7.29 (m, 2H), 7.35 (d, J = 8.8 Hz, 4H), 7.40 (d, J = 8.8 Hz, 4H), 7.42 (d, J = 8.8 Hz, 4H), 7.50 (m, 4H), 7.61–7.66 (m, 2H), 7.89 (d, J = 8.1 Hz, 4H), 8.19–8.22 (m, 5H), 8.29 (s, 2H), 8.32 (s, 2H), 8.39 (m, 2H), 8.48 (d, J = 8.1 Hz, 2H), 8.82 (d, J = 4.4 Hz, 2H), 8.89 (d, J = 5.1 Hz, 2H), 8.96 (d, J = 5.1 Hz, 2H), 9.03 (d, J = 5.1 Hz, 2H), 9.24 (d, J = 8.8 Hz, 2H), 9.44 (d, J = 8.1 Hz, 2H); MALDI-MS (dithranol) obsd 2664.25 [M^+], 2517.33 [$(M - 4\text{-}t\text{-BuPhO})^+$], 1900.24 [$(M - \text{perylene})^+$], calcd 2664.62 ($C_{183}H_{156}N_6O_{10}Zn$); λ_{abs} 427, 541 nm; λ_{em} (λ_{ex} = 540 nm) 599, 647 nm.

1-(4-Ethynylbenzoyl)-9-(4-iodobenzoyl)-5-mesityldipyrromethane (17)

A sample of **16** (300 mg, 0.432 mmol) in $CHCl_3$ (10 mL) was treated with TBAF on silica (648 mg, 1.0–1.5 mmol F^-/g resin) at room temperature for 1 h. The mixture was washed with 10% $NaHCO_3$. The organic phase was washed with water, dried (Na_2SO_4), and concentrated. Column chromatography [silica, CH_2Cl_2–ethyl acetate (95 : 5)] afforded a brown solid (262 mg, 97%): mp 106–108 °C; ^1H NMR δ 2.24 (s, 6H), 2.32 (s, 3H), 3.18 (s, 1H), 5.95 (m, 2H), 6.21 (s, 1H), 6.56–6.60 (m, 2H), 6.93 (s, 2H), 7.40 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 8.1 Hz, 2H), 7.64 (d, J = 8.1 Hz, 2H), 7.72 (d, J = 8.1 Hz, 2H), 11.40 (m, 2H); ^{13}C NMR δ 21.0, 39.4, 79.7, 83.2, 99.1, 110.9, 121.3, 121.4, 125.5, 129.4, 130.2, 130.3, 130.5, 131.0, 131.9, 133.1, 137.3, 137.4, 137.6, 138.3, 140.6, 140.7, 182.9; HRMS (FAB) obsd 623.1186, calcd 623.1196. Anal. calcd for $C_{34}H_{27}IN_2O_2$: C, 65.60; H, 4.37; N, 4.50. Found: C, 65.52; H, 4.72; N, 4.31%.

Zn(II)–5-[3,5-Bis(2-{4-[1,6,9-tris(4-*tert*-butylphenoxy)perylene-3,4-dicarboximido]-3,5-diisopropylphenyl}ethynyl)phenyl]-10-(4-iodophenyl)-15-mesityl-20-(4-ethynylphenyl)porphyrin (18)

Following a known procedure[46] with improved acid catalysis conditions,[45] a sample of **17** (26 mg, 41 μmol) was reduced with $NaBH_4$ (30 mg, 0.82 mmol) in THF–methanol [5.0 mL (10 : 1)]. The resulting dipyrromethane-dicarbinol was condensed with **13** (86 mg, 41 μmol) in CH_2Cl_2 (16 mL) containing $Yb(OTf)_3$ (32 mg, 51 μmol, 3.2 mM) for 20 min. DDQ (28 mg, 120 μmol) was added and the mixture was stirred at room temperature for 1 h. The mixture was neutralized with TEA then filtered through a silica column [CH_2Cl_2–hexanes (2 : 1)]. The residue was treated with $Zn(OAc)_2{\cdot}2H_2O$ (46 mg, 210 μmol) in CH_2Cl_2 (10 mL) and methanol (3.0 mL) at room temperature for 15 h. The reaction mixture was washed with water and dried (Na_2SO_4). The mixture was passed through a silica gel column [CH_2Cl_2–hexanes (2 : 1)] followed by trituration with methanol to afford a red solid (33.5 mg, 30%): ^1H NMR δ 1.13 (d, J = 6.6 Hz, 24H), 1.30 (s, 18H), 1.33 (s, 18H), 1.34 (s, 18H), 1.83 (s, 6H), 2.64–2.72 (m, 7H), 3.31 (s, 1H), 6.89 (d, J = 8.8 Hz, 2H), 7.01 (d, J = 8.8 Hz, 4H), 7.06 (d, J = 8.8 Hz, 4H), 7.08 (d, J = 8.8 Hz, 4H), 7.29 (m, 2H), 7.35 (d, J = 8.8 Hz, 4H), 7.40 (d, J = 8.1 Hz, 4H), 7.41 (d, J = 8.1 Hz, 4H), 7.50 (m, 4H), 7.60–7.66 (m, 2H), 7.89 (d, J = 8.1 Hz, 2H), 7.97 (d, J = 8.1 Hz, 2H), 8.10 (d, J = 8.8 Hz, 2H), 8.19–8.23 (m, 3H), 8.29 (s, 2H), 8.32 (s, 2H), 8.39 (m, 2H), 8.47 (d, J = 8.1 Hz, 2H), 8.81 (d, J = 4.4 Hz, 2H), 8.88–8.90 (m, 2H), 8.96 (d, J = 5.1 Hz, 2H), 9.03 (d, J = 5.1 Hz, 2H), 9.24 (d, J = 8.8 Hz, 2H), 9.44 (d, J = 8.1 Hz, 2H); MALDI-MS (dithranol) obsd 2760.44 [M^+], 2634.37 [$(M - I)^+$], calcd 2766.50 ($C_{181}H_{155}IN_6O_{10}Zn$); λ_{abs} 427, 542 nm; λ_{em} (λ_{ex} = 540 nm) 598, 647 nm.

Zn(II)–5,15-Bis[3,5-bis(2-{4-[1,6,9-tris(4-*tert*-butylphenoxy)perylene-3,4-dicarboximido]-3,5-diisopropylphenyl}ethynyl)phenyl]-10,20-bis(4-ethynylphenyl)porphyrin (22)

Following a known procedure,[49] samples of **21** (6.1 mg, 47 μmol) and **13** (100 mg, 47 μmol) were condensed in CH_2Cl_2 (4.7 mL) containing TFA (6.5 μL, 84 μmol) at room temperature for 1 h. Then DDQ (16 mg, 71 μmol) was added. After 1 h, TEA was added and the crude mixture was passed through a silica column [CH_2Cl_2–hexanes (2 : 1)] followed by preparative SEC (THF). The residue was treated with $Zn(OAc)_2{\cdot}2H_2O$ (53 mg, 240 μmol) in CH_2Cl_2 (8.0 mL) and methanol (2.0 mL) at room temperature for 15 h. The organic phase was washed with water, dried (Na_2SO_4), and concentrated. Column chromatography [silica, CH_2Cl_2–hexanes (2 : 1)] followed by trituration with methanol afforded a red solid (24.1 mg, 23%): ^1H NMR δ 1.13 (d, J = 6.6 Hz, 48H), 1.30 (s, 36H), 1.33 (s, 36H), 1.34 (s, 36H), 2.65–2.74 (m, 8H), 3.32 (s, 2H), 6.88 (d, J = 8.8 Hz, 4H), 7.01 (d, J = 8.8 Hz, 8H), 7.07 (d, J = 8.1 Hz, 8H), 7.08 (d, J = 8.8 Hz, 8H), 7.35 (d, J = 8.8 Hz, 8H), 7.40 (d, J = 8.8 Hz, 8H), 7.42 (d, J = 8.8 Hz, 8H), 7.50 (m, 8H), 7.60–7.66 (m, 4H), 7.91 (d, J = 8.1 Hz, 4H), 8.20–8.23 (m, 6H), 8.29 (s, 4H), 8.32 (s, 4H), 8.40–8.41 (m, 4H), 8.47 (d, J = 8.8 Hz, 4H), 9.00 (d, J = 4.4 Hz, 4H), 9.06 (d, J = 4.4 Hz, 4H), 9.24 (d, J = 8.8 Hz, 4H), 9.44 (d, J = 7.3 Hz, 4H); MALDI-MS (dithranol) obsd 4515.17 [M^+], 4390.09 [$(M - 4\text{-}t\text{-BuPhO})^+$], 3756.60 [$(M - \text{perylene})^+$], calcd 4518.93 ($C_{312}H_{272}N_8O_{20}Zn$); λ_{abs} 429, 539 nm; λ_{em} (λ_{ex} = 540 nm) 600, 649 nm.

Zn(II)–5,15-Bis[3,5-bis(2-{4-[1,6,9-tris(4-*tert*-butylphenoxy)perylene-3,4-dicarboximido]-3,5-diisopropylphenyl}ethynyl)phenyl]porphyrin (24)

Following a general procedure,[49] samples of **23** (14.6 mg, 99.9 μmol) and **12** (200 mg, 99.9 μmol) in CH_2Cl_2 (10 mL) were condensed in the presence of TFA (13.7 μL, 178 μmol) at room temperature for 30 min. DDQ (34.0 mg, 150 μmol) was then added. After 1 h, the reaction mixture was passed through a silica column [CH_2Cl_2–hexanes (4 : 1)]. The crude free base porphyrin was dissolved in $CHCl_3$ (15 mL) and treated with $Zn(OAc)_2{\cdot}2H_2O$ (54.8 mg, 250 μmol) in MeOH (2 mL) at room temperature for 12 h. The reaction mixture was passed through a silica column ($CHCl_3$) to afford a magenta solid (93.6 mg, 43%): ^1H NMR δ 1.14 (d, J = 6.4 Hz, 48H), 1.30 (s, 36H), 1.33 (s, 36H), 1.34 (s, 36H), 2.70 (m, 8H), 6.88 (d, J = 9.2 Hz, 4H), 7.00 (d, J = 8.4 Hz, 8H), 7.05–7.10 (m, 16H), 7.35 (d, J = 8.4 Hz, 8H), 7.38–7.42 (m, 16H), 7.52 (s, 8H), 7.63 (t, J = 8.4 Hz, 4H), 8.26–8.32 (m, 10H), 8.46–8.48 (m, 8H), 9.23 (d, J = 4.8 Hz, 4H), 9.25 (s, 4H), 9.43 (d, J = 7.6 Hz, 4H), 9.54 (d, J = 4.4 Hz, 4H), 10.41 (s, 2H); LD-MS obsd 4308.53, calcd avg. mass 4318.70 ($C_{296}H_{264}N_8O_{20}Zn$); λ_{abs} 418, 539 nm; λ_{em} (λ_{ex} = 540 nm) 580, 631 nm.

Zn(II)–5,15-Bis[3,5-bis(2-{4-[1,6,9-tris(4-*tert*-butylphenoxy)perylene-3,4-dicarboximido]-3,5-diisopropylphenyl}ethynyl)phenyl]-10,20-dibromoporphyrin (25)

Following a standard procedure,[50] a sample of **24** (93.0 mg, 21.6 μmol) was dissolved in $CHCl_3$ (5.5 mL) and cooled to 0 °C. Pyridine (12 μL) was added followed by NBS (7.7 mg, 43.2 μmol, recrystallized from H_2O). The reaction mixture was stirred at 0 °C for 30 min, warmed to room temperature, then passed through a silica column [CH_2Cl_2–hexanes (4 : 1)]. The resulting magenta solid was triturated with methanol, then hexanes to recover a magenta solid (69.4 mg, 72%): ^{1}H NMR δ 1.14 (d, J = 6.4 Hz, 48H), 1.31 (s, 36H), 1.33 (s, 36H), 1.34 (s, 36H), 2.71 (m, 8H), 6.88 (d, J = 9.2 Hz, 4H), 7.00 (d, J = 8.4 Hz, 8H), 7.06–7.10 (m, 16H), 7.36 (d, J = 8.4 Hz, 8H), 7.39–7.43 (m, 16H), 7.52 (s, 8H), 7.63 (t, J = 8.4 Hz, 4H), 8.25–8.35 (m, 10H), 8.46–8.48 (d, J = 8.0 Hz, 8H), 9.05 (d, J = 4.8 Hz, 4H), 9.24 (s, 4H), 9.43 (d, J = 7.6 Hz, 4H), 9.81 (d, J = 4.4 Hz, 4H); LD-MS obsd 4467.11, calcd avg. mass 4476.49 ($C_{296}H_{262}Br_2N_8O_{20}Zn$); λ_{abs} 435, 537, 598 nm.

1,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (26)

Following a standard procedure,[56,62] samples of 1,4-bis(dihydroxyboryl)benzene (5.16 g, 31.1 mmol) and pinacol (8.83 g, 74.7 mmol) were dissolved in anhydrous DMF (100 mL). The reaction mixture was stirred for 12 h at room temperature, affording a white solid. Water (100 mL) was added and the reaction mixture was filtered. The resulting white solid was then recrystallized from ethyl acetate affording white needles (9.23 g, 93%). Physical data for this compound are identical to the literature.[63]

Synthesis of oligomers

Oligo-6. Samples of **6** (8.0 mg, 5.6 μmol), $Pd(PPh_3)_2Cl_2$ (0.50 mg, 0.75 μmol), CuI (70 μg, 0.36 μmol) and I_2 (1.4 mg, 5.6 μmol) were dissolved in toluene–DIEA [2.2 mL (5 : 1)]. The reaction mixture was stirred in air at room temperature overnight. Analysis by SEC showed very little starting monomer with most of the material exhibiting significantly higher molecular weight. The solvent was removed yielding a film that was intractable. Further analysis was not attempted.

Oligo-15. A solution of **15** (20 mg, 7.5 μmol) in toluene–DIEA [3.0 mL (5 : 1)] was treated with $Pd(PPh_3)_2Cl_2$ (1.0 mg, 1.5 μmol), CuI (0.3 mg, 2 μmol) and I_2 (1.9 mg, 7.5 μmol). The mixture was stirred in air at room temperature for 2 h. THF was added (8 mL) and the mixture was passed over a preparative SEC column (THF). The leading band was collected and concentrated. The resulting material was passed over a silica column ($CHCl_3$). The major band was concentrated and the resulting solid was washed with methanol and then hexanes. The sample was dried yielding a magenta film (11.1 mg, 56%): ^{1}H NMR δ 1.29 (s, 18H), 1.32 (s, 18H), 1.34 (s, 18H), 1.78 (m, 6H), 2.62–2.75 (m, 7H), 6.9 (d, 2H), 7.00–7.09 (m, 12H), 7.34–7.43 (m, 14H), 7.62 (t, 2H), 8.0 (br s, 4H), 8.23–8.33 (m, 9H), 8.44–8.49 (m, 4H), 8.86 (br s, 2H), 8.88 (br s, 2H), 9.04 (br s, 2H), 9.08 (br s, 2H), 9.24 (d, 2H), 9.45 (d, 2H); λ_{abs} 430, 438, 547, 598 nm; λ_{em} (λ_{ex} = 500 nm) 609, 654 nm.

Oligo-18. A mixture of **18** (20 mg, 7.2 μmol), $Pd_2(dba)_3$ (1.0 mg, 1.1 μmol) and Ph_3As (2.7 mg, 8.7 μmol) in toluene–TEA [3.0 mL (5 : 1)] was stirred under Ar at room temperature. Aliquots were removed and analyzed by SEC after 2 h, 5 h, and 22 h. The reaction was stopped after 23 h. The reaction mixture was concentrated to near dryness. THF was added and the reaction mixture was passed through a preparative SEC column (THF). The leading band was collected and concentrated. The resulting solid was triturated with methanol, then hexanes yielding a magenta solid (16.8 mg, 88%): ^{1}H NMR δ 1.29 (s, 18H), 1.32 (s, 18H), 1.34 (s, 18H), 1.78 (m, 6H), 2.62–2.75 (m, 7H), 6.88 (d, 2H), 7.00–7.09 (m, 12H), 7.34–7.40 (m, 12H), 7.53 (d, 2H), 7.62 (t, 2H), 8.10 (br s, 4H), 8.29–8.32 (m, 9H), 8.46 (d, 4H), 8.88 (br s, 2H), 9.04 (br s, 2H), 9.11 (br s, 2H), 9.23 (d, 2H), 9.43 (d, 2H); λ_{abs} 429, 540, 595 nm; λ_{em} (λ_{ex} = 429 nm) 604, 652 nm.

Oligo-22. Samples of **22** (7.8 mg, 1.7 μmol), $Pd(PPh_3)_2Cl_2$ (0.24 mg, 0.34 μmol) and CuI (0.07 mg, 0.3 μmol) were dissolved in toluene–DIEA [0.70 mL (9 : 1)]. The mixture was stirred under an air atmosphere at room temperature for 1 h. Additional toluene was added and the crude mixture was washed with saturated aqueous NH_4Cl. The organic layer was dried (Na_2SO_4) and concentrated. Column chromatography (silica, $CHCl_3$) followed by trituration with methanol afforded a magenta solid (6.2 mg, 81%). ^{1}H NMR integration was not attempted. λ_{abs} 434, 537, 595 nm; λ_{em} (λ_{ex} = 429 nm) 605, 652 nm.

Attempted synthesis of oligo-25

Samples of **25** (40 mg, 4.5 μmol), **26** (2.9 mg, 4.5 μmol), $Pd(PPh_3)_4$ (3.1 mg, 1.3 μmol) and K_2CO_3 (9.8 mg, 36 μmol) were dissolved in toluene–DMF [900 μL (2 : 1)]. The reaction mixture was placed into an oil bath heated to 90 °C and stirred for 48 h. Analytical SEC analysis did not show the presence of sizable oligomers.

Acknowledgements

This research was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy. Mass spectra were obtained at the Mass Spectrometry Laboratory for Biotechnology at North Carolina State University. Partial funding for the Facility was obtained from the North Carolina Biotechnology Center and the National Science Foundation.

References

1 R. S. Loewe, R. K. Lammi, J. R. Diers, C. Kirmaier, D. F. Bocian, D. Holten and J. S. Lindsey, *J. Mater. Chem.*, 2002, **12**, 1530.
2 S. E. Webber, *Chem. Rev.*, 1990, **90**, 1469.
3 (*a*) G. F. Strouse, L. A. Worl, J. N. Younathan and T. J. Meyer, *J. Am. Chem. Soc.*, 1989, **111**, 9101; (*b*) M. Sykora, K. A. Maxwell, J. M. DeSimone and T. J. Meyer, *Proc. Natl. Acad. Sci. USA*, 2000, **97**, 7687.
4 (*a*) D. M. Watkins and M. A. Fox, *J. Am. Chem. Soc.*, 1994, **116**, 6441; (*b*) B. Hong and M. A. Fox, *Can. J. Chem.*, 1995, **73**, 2101.
5 D. Holten, D. F. Bocian and J. S. Lindsey, *Acc. Chem. Res.*, 2002, **35**, 57.
6 M. del Rosario Benites, T. E. Johnson, S. Weghorn, L. Yu, P. D. Rao, J. R. Diers, S. I. Yang, C. Kirmaier, D. F. Bocian, D. Holten and J. S. Lindsey, *J. Mater. Chem.*, 2002, **12**, 65.
7 A. Ambroise, C. Kirmaier, R. W. Wagner, R. S. Loewe, D. F. Bocian, D. Holten and J. S. Lindsey, *J. Org. Chem.*, 2002, **67**, 3811.
8 A. K. Burrell, D. L. Officer, P. G. Plieger and D. C. W. Reid, *Chem. Rev.*, 2001, **101**, 2751.
9 (*a*) D. Wöhrle and G. Krawczyk, *Makromol. Chem.*, 1986, **187**, 2535; (*b*) D. Wöhrle and M. Paliuras, *Makromol. Chem.*, 1991, **192**, 819; (*c*) A. Kajiwara, K. Aramata, S. Nomura, Y. Morishima and M. Kamachi, *Chem. Lett.*, 1992, 95; (*d*) H. Aota, Y. Itai, A. Matsumoto and M. Kamachi, *Chem. Lett.*, 1994, 2043; (*e*) S. Salhi, S. Kulikov, C. Bied-Charreton and J. P. Galaup, *Laser Chem.*, 1996, **16**, 219; (*f*) W. R. Trumble, *J. Heterocycl. Chem.*, 1997, **34**, 999; (*g*) F. Feng, T. Miyashita, Y. Amao and K. Asai, *Thin Solid Films*, 2000, **366**, 255; (*h*) M. Nowakowska, A. Karewicz, N. Loukine and J. E. Guillet, *Polymer*, 2002, **43**, 2003.
10 T. Shimidzu, *Synth. Met.*, 1996, **81**, 235.
11 E. Scamporrino and D. Vitalini, *Macromolecules*, 1992, **25**, 1625.
12 (*a*) B. Jiang, S.-W. Yang and W. E. Jones Jr., *Chem. Mater.*, 1997, **9**, 2031; (*b*) B. Jiang and W. E. Jones Jr., *Macromolecules*, 1997, **30**, 5575; (*c*) B. Jiang, S.-W. Yang, R. Niver and W. E. Jones Jr., *Synth. Met.*, 1998, **94**, 205; (*d*) B. Jiang, S. W. Yang, S. L. Bailey, L. G. Hermans, R. A. Niver, M. A. Bolcar and W. E. Jones Jr., *Coord. Chem. Rev.*, 1998, **171**, 365; (*e*) D. M. Sarno, B. Jiang, D. Grosfeld, J. O. Afriyie, L. J. Matienzo and W. E. Jones Jr., *Langmuir*, 2000, **16**, 6191; (*f*) D. M. Sarno, L. J. Matienzo and W. E. Jones Jr., *Inorg. Chem.*, 2001, **40**, 6308.
13 Q. Wang, L. Wang, J. Yu and L. Yu, *Adv. Mater.*, 2000, **12**, 974.

14 H. Ohkita, T. Ogi, R. Kinoshita, S. Ito and M. Yamamoto, *Polymer*, 2002, **43**, 3571.

15 (*a*) H. L. Anderson, *Inorg. Chem.*, 1994, **33**, 972; (*b*) K. Pichler, H. L. Anderson, D. D. C. Bradley, R. H. Friend, P. J. Hamer, M. G. Harrison, C. P. Jarrett, S. J. Martin and J. A. Stephens, *Mol. Cryst. Liq. Cryst.*, 1994, **256**, 415.

16 P. N. Taylor, J. Huuskonen, G. Rumbles, R. T. Aplin, E. Williams and H. L. Anderson, *Chem. Commun.*, 1998, 909.

17 T. E. O. Screen, K. B. Lawton, G. S. Wilson, N. Dolney, R. Ispasoiu, T. Goodson III, S. J. Martin, D. D. C. Bradley and H. L. Anderson, *J. Mater. Chem.*, 2001, **11**, 312.

18 B. Jiang, S.-W. Yang, D. C. Barbini and W. E. Jones Jr., *Chem. Commun.*, 1998, 213.

19 T. Yamamoto, N. Fukushima, H. Nakajima, T. Maruyama and I. Yamaguchi, *Macromolecules*, 2000, **33**, 5988.

20 A. Ferri, G. Polzonetti, S. Licoccia, R. Paolesse, D. Favretto, P. Traldi and M. V. Russo, *J. Chem. Soc., Dalton Trans.*, 1998, 4063.

21 N. Aratani, A. Osuka, Y. H. Kim, D. H. Jeong and D. Kim, *Angew. Chem., Int. Ed.*, 2000, **39**, 1458.

22 N. Aratani and A. Osuka, *Macromol. Rapid Commun.*, 2001, **22**, 725.

23 A. Nakano, T. Yamazaki, Y. Nishimura, I. Yamazaki and A. Osuka, *Chem. Eur. J.*, 2000, **6**, 3254.

24 A. Tsuda and A. Osuka, *Science*, 2001, **293**, 79.

25 (*a*) M. J. Crossley and P. L. Burn, *J. Chem. Soc., Chem. Commun.*, 1987, 39; (*b*) H. Tamiaki, S. Suzuki and K. Maruyama, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 2633.

26 J. S. Lindsey and R. W. Wagner, *J. Org. Chem.*, 1989, **54**, 828.

27 R. W. Wagner, J. S. Lindsey, I. Turowska-Tyrk and W. R. Scheidt, *Tetrahedron*, 1994, **50**, 11097.

28 S. Prathapan, T. E. Johnson and J. S. Lindsey, *J. Am. Chem. Soc.*, 1993, **115**, 7519.

29 J. Li, A. Ambroise, S. I. Yang, J. R. Diers, J. Seth, C. R. Wack, D. F. Bocian, D. Holten and J. S. Lindsey, *J. Am. Chem. Soc.*, 1999, **121**, 8927.

30 (*a*) R. W. Wagner and J. S. Lindsey, *Pure Appl. Chem.*, 1996, **68**, 1373; (*b*) R. W. Wagner and J. S. Lindsey, *Pure Appl. Chem.*, 1998, **70**(8), i.

31 R. S. Loewe, K.-Y. Tomizaki, F. Chevalier and J. S. Lindsey, manuscript in preparation.

32 S. Prathapan, S. I. Yang, J. Seth, M. A. Miller, D. F. Bocian, D. Holten and J. S. Lindsey, *J. Phys. Chem. B*, 2001, **105**, 8237.

33 S. I. Yang, S. Prathapan, M. A. Miller, J. Seth, D. F. Bocian, J. S. Lindsey and D. Holten, *J. Phys. Chem. B*, 2001, **105**, 8249.

34 S. I. Yang, R. K. Lammi, S. Prathapan, M. A. Miller, J. Seth, J. R. Diers, D. F. Bocian, J. S. Lindsey and D. Holten, *J. Mater. Chem.*, 2001, **11**, 2420.

35 C. Kirmaier, S. I. Yang, S. Prathapan, M. A. Miller, J. R. Diers, D. F. Bocian, J. S. Lindsey and D. Holten, *Res. Chem. Intermed.*, in press.

36 K.-Y. Tomizaki, R. S. Loewe, C. Kirmaier, J. K. Schwartz, J. L. Retsek, D. F. Bocian, D. Holten and J. S. Lindsey, *J. Org. Chem.*, 2002, **67**, in press.

37 (*a*) H. Langhals, C. Wagner and R. Ismael, *New J. Chem.*, 2001, **25**, 1047; (*b*) J. Hofkens, L. Latterini, G. De Belder, T. Gensch, M. Maus, T. Vosch, Y. Karni, G. Schweitzer, F. C. De Schryver, A. Hermann and K. Müllen, *Chem. Phys. Lett.*, 1999, **304**, 1; (*c*) M. Lor, R. De, S. Jordens, G. De Belder, G. Schweitzer, M. Cotlet, J. Hofkens, T. Weil, A. Herrmann, K. Müllen, M. Van Der Auweraer and F. C. De Schryver, *J. Phys. Chem. A*, 2002, **106**, 2083.

38 H. Langhals, *Chem. Ber.*, 1985, **118**, 4641.

39 W. E. Ford and P. V. Kamat, *J. Phys. Chem.*, 1987, **91**, 6373.

40 (*a*) A. Rademacher, S. Märkle and H. Langhals, *Chem. Ber.*, 1982, **115**, 2927; (*b*) E. M. Ebeid, S. A. El-Daly and H. Langhals, *J. Phys. Chem.*, 1988, **92**, 4565.

41 S. I. Yang, R. K. Lammi, J. Seth, J. A. Riggs, T. Arai, D. Kim, D. F. Bocian, D. Holten and J. S. Lindsey, *J. Phys. Chem. B*, 1998, **102**, 9426.

42 W. J. Youngblood, D. T. Gryko, R. K. Lammi, J. R. Diers, D. F. Bocian, D. Holten and J. S. Lindsey, *J. Org. Chem.*, 2002, **67**, 2111.

43 L. Yu, K. Y. Tomizaki and J. S. Lindsey, manuscript in preparation.

44 B. J. Littler, M. A. Miller, C.-H. Hung, R. W. Wagner, D. F. O'Shea, P. D. Boyle and J. S. Lindsey, *J. Org. Chem.*, 1999, **64**, 1391.

45 G. R. Geier III, J. B. Callinan, P. D. Rao and J. S. Lindsey, *J. Porphyrins Phthalocyanines*, 2001, **5**, 810.

46 P. D. Rao, S. Dhanalekshmi, B. J. Littler and J. S. Lindsey, *J. Org. Chem.*, 2000, **65**, 7323.

47 P. D. Rao, B. J. Littler, G. R. Geier III and J. S. Lindsey, *J. Org. Chem.*, 2000, **65**, 1084.

48 W. B. Austin, N. Bilow, W. J. Kelleghan and K. S. Y. Lau, *J. Org. Chem.*, 1981, **46**, 2280.

49 B. J. Littler, Y. Ciringh and J. S. Lindsey, *J. Org. Chem.*, 1999, **64**, 2864.

50 S. G. DiMagno, V. S.-Y. Lin and M. J. Therien, *J. Org. Chem.*, 1993, **58**, 5983.

51 Q. Liu and D. J. Burton, *Tetrahedron Lett.*, 1997, **38**, 4371.

52 R. W. Wagner, T. E. Johnson, F. Li and J. S. Lindsey, *J. Org. Chem.*, 1995, **60**, 5266.

53 (*a*) X. Zhou, Z.-Y. Zhou, T. C. W. Mak and K. S. Chan, *J. Chem. Soc., Perkin Trans. 1*, 1994, 2519; (*b*) K. S. Chan, X. Zhou, B.-S. Luo and T. C. W. Mak, *J. Chem. Soc., Chem. Commun.*, 1994, 271; (*c*) X. Zhou, M. K. Tse, T. S. M. Wan and K. S. Chan, *J. Org. Chem.*, 1996, **61**, 3590; (*d*) M. K. Tse, Z.-Y. Zhou, T. C. W. Mak and K. S. Chan, *Tetrahedron*, 2000, **56**, 7779.

54 (*a*) N. Yoshida, H. Shimidzu and A. Osuka, *Chem. Lett.*, 1998, 55; (*b*) D. A. Shultz, K. P. Gwaltney and H. Lee, *J. Org. Chem.*, 1998, **63**, 769; (*c*) A. G. Hyslop, M. A. Kellett, P. M. Iovine and M. J. Therien, *J. Am. Chem. Soc.*, 1998, **120**, 12676; (*d*) M. Kimura, T. Shiba, T. Muto, K. Hanabusa and H. Shirai, *Macromolecules*, 1999, **32**, 8237; (*e*) C. M. Muzzi, C. J. Medforth, L. Voss, M. Cancilla, C. Lebrilla, J.-G. Ma, J. A. Shelnutt and K. M. Smith, *Tetrahedron Lett.*, 1999, **40**, 6159; (*f*) Y. Deng, C. K. Chang and D. G. Nocera, *Angew. Chem., Int. Ed.*, 2000, **39**, 1066; (*g*) B. Vaz, R. Alvarez, M. Nieto, A. I. Paniello and A. R. de Lera, *Tetrahedron Lett.*, 2001, **42**, 7409; (*h*) N. Aratani and A. Osuka, *Org. Lett.*, 2001, **3**, 4213; (*i*) H. Uno, Y. Kitawaki and N. Ono, *Chem. Commun.*, 2002, 116.

55 (*a*) X. Zhou and K. S. Chan, *J. Org. Chem.*, 1998, **63**, 99; (*b*) X. Zhou and K. S. Chan, *J. Chem. Soc., Chem., Commun.*, 1994, 2493.

56 L. Yu and J. S. Lindsey, *Tetrahedron*, 2001, **57**, 9285.

57 A. Osuka, N. Tanabe, S. Nakajima and K. Maruyama, *J. Chem. Soc., Perkin Trans. 2*, 1996, 199.

58 A. A. Bothner-By, J. Dadok, T. E. Johnson and J. S. Lindsey, *J. Phys. Chem.*, 1996, **100**, 17551.

59 P. G. Seybold and M. Gouterman, *J. Mol. Spectrosc.*, 1969, **31**, 1.

60 T. M. Swager, *Acc. Chem. Res.*, 1998, **31**, 201.

61 (*a*) D. Fenyo, B. T. Chait, T. E. Johnson and J. S. Lindsey, *J. Porphyrins Phthalocyanines*, 1997, **1**, 93; (*b*) N. Srinivasan, C. A. Haney, J. S. Lindsey, W. Zhang and B. T. Chait, *J. Porphyrins Phthalocyanines*, 1999, **3**, 283.

62 (*a*) M. Nicolas, B. Fabre, G. Marchand and J. Simonet, *Eur. J. Org. Chem.*, 2000, 1703; (*b*) T. Ishiyama, Y. Itoh, T. Kitano and N. Miyaura, *Tetrahedron Lett.*, 1997, **38**, 3447.

63 D. A. Shultz, H. Lee, R. K. Kumar and K. P. Gwaltney, *J. Org. Chem.*, 1999, **64**, 9124.