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Full Paper

Efficient Synthesis of Novel Porphyrin Dimers with Versatile Linkers via Bis(dipyrromethanes) in an Excellent Mixed-Solvent

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A general and efficient protocol has been developed to synthesise a series of novel porphyrin dimers with versatile aryl linkers via a simultaneous condensation-cyclisation-oxidation reaction of diverse bis(dipyrromethanes) with dipyrromethane-dicarbinol catalysed by indium(III) chloride at room temperature in an efficient CH_2Cl_2 and CH_3CN mixed-solvent. The reaction yields increased to 21–26 % based on liquid chromatography-mass spectrometry (LCMS) and isolated yields were 13–19 % due to the use of the proper mixed-solvent. This mild method is applicable to the preparation of linker-tunable porphyrin dimers with targeted functionalities and could potentially be extended to the single-step construction of longer functionalised multiporphyrin arrays.

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Introduction

Covalently linked multiporphyrin arrays have continued to be synthesised and fabricated for use in molecular devices owing to their special electronic structures.[1–3] A key factor influencing the properties and functionality of these compounds is the electronic interaction between both the constituent porphyrin rings and the embedded linkers.[2,4] Therefore, diverse porphyrin dimers or multiporphyrin arrays are urgently required for basic properties research. However, this task has been seriously restricted by inefficient synthetic techniques. Recently, considerable attention has been paid to binding multiple porphyrin units into functionalised arrays using numerous types of linkers in a simple, feasible way.[5] The typical method for constructing multiporphyrin arrays is to couple intact porphyrin building blocks.[6] However, this inconvenient stepwise approach only introduces fixed linkers into the porphyrin backbones, which severely limits the possible diversity and functionality of the multiporphyrin arrays. Another approach is the '2+2' method first reported by MacDonald[7] and exploited by Lindsey.[8] This method is a well known and potentially important strategy because the key intermediate compound in this method, bis (dipyrromethanes) can be designed to contain changeable linkers that can then, theoretically, be condensed in one step to afford diverse multiporphyrin arrays with targeted functionality. However, to the best of our knowledge, only a few porphyrin dimers have been produced via this '2+2' method with yields below 8 %,[8] and multiporphyrin arrays containing more porphyrin units have not yet been obtained due in part to the competing reaction between the α and β positions on pyrrole during the dipyrromethane-dicarbinol[9] and bis(dipyrromethanes) acidolysis reactions.[10] The '2+2' method for the facile construction of multiporphyrin arrays urgently requires modification for further investigations and applications.

To this end, we developed a protocol in an earlier work in 2010 for preparing the key intermediates, bis(dipyrromethanes), and obtained one porphyrin dimer in a 12 % yield by modifying the '2+2' method.[11] In this report, we further modify the '2+2' method by using a CH_2Cl_2/CH_3CN mixed-solvent to synthesise a series of novel porphyrin dimers, bearing various linkers in the middle and two active groups at the termini, in satisfactory yields. This protocol should be applicable to the construction of longer multiporphyrin arrays, such as porphyrin trimers, tetramers, pentamers and so on. Therefore, our work offers a chance to further study the synthesis of multiporphyrin compounds and exploit advances in their promising applications.

Results and Discussion

With the ultimate objective of developing an efficient and general method for constructing porphyrin dimers for basic photoelectric performance research, nine types of linked bis (dipyrromethanes), **3**, were selected for this work. For example, both conjugated linkers with different conjugation lengths, such as phenylene, biphenylene, triphenylene, and triphenylenevinylene, and non-conjugated linkers, such as diphenylether and 1,4-diphenoxybenzene, were included. In addition, three types of classical photoelectric materials, triphenyl amine, carbazole, and diphenyl fluorene, were introduced as linkers. These linkers

endowed the porphyrin dimers with different distances between the adjacent porphyrin rings. Moreover, all of these linkers provide diverse steric configurations with different spatial positions between the porphyrin units. For example, phenylene, biphenylene, and triphenylene make the whole molecular structure linear, while triphenyl amine makes it pyramidal, where the two porphyrin planes present different dihedral angles in these latter porphyrin dimers.[12] In addition to the above, porphyrin dimers substituted with -Br at the termini are functionalised for further Suzuki or Heck coupling and such dimers can be readily converted into advanced functional molecules such as porphyrinic macrocycle-polymers[13] or photosensitive dyes.[14] From a synthetic standpoint, the applied protocol for constructing porphyrin dimers using such versatile and challenging linked bis(dipyrromethanes), **3**, may be considered general, and the relatively high efficiency may be considered an advancement relative to those previously reported.

With these advantages in mind, a series of phenylene-, biphenylene-, triphenylene-, triphenylenevinylene-, diphenylether-, 1,4-diphenoxy-benzene-, carbazole-, triphenyl amine-, and diphenyl fluorene-linked dialdehydes, **1**, was first prepared. We used an alkylation-bromomethylation-acetylation-reduction-oxidation-Wittig reaction to transform 1,4-hydroquinone into the phenylene-linked dialdehydes (**1a**–**1c**), triphenylenevinylene-linked dialdehydes (**1g**–**1h**) and diphenyl fluorene-linked dialdehyde (**1m**).[11,15] Both a Miyaura cross-coupling and Suzuki coupling reaction or a Suzuki bis-coupling reaction were used to synthesise the biphenylene-linked dialdehydes (**1d**–**1e**) and triphenylene-linked dialdehyde (**1f**).[11] The diphenylether-linked dialdehyde (**1i**) and 1,4-diphenoxybenzene-linked dialdehyde (**1j**) were synthesised via a condensation reaction between either 4-bromobenzaldehyde and 4-hydroxybenzene or 4,4′-dihydroxybenzene,[16] and dialdehyde **1l** was obtained via the oxidation of *N*,*N*-diphenyl-4-bromophenylamine by $POCl_3$.[17]

With this library of dialdehydes in hand, our attention shifted to the synthesis of the important bis(dipyrromethane) intermediates, **3**. Scheme 1 illustrates this synthesis, which used identical or slightly modified synthetic conditions to those reported by our group.[11] A neat reaction between pyrrole and the above synthesised dialdehydes (160 : 1) was catalysed by $InCl_3$ (0.2 equiv.) at room temperature for 30 min. After a simple purification, the corresponding bis(dipyrromethanes), **3**, were readily obtained in satisfactory yields (>80 %) and high quality.

With these novel bis(dipyrromethanes) in hand, we focussed on finding an efficient synthetic strategy for constructing versatile porphyrin dimers. In our previous work, we established a condensation-cyclisation-oxidation reaction model for the facile construction of porphyrin dimers, which involves the $InCl_3$-catalysed condensation of a bis(dipyrromethane), **3a** (1.0 equiv.) with dipyrromethane-dicarbinol, **4** (3.0 equiv.), followed by an oxidation using 2,3,5,6- tetrachlorocyclohexa-2,5-diene-1,4-dione (Chloranil, 5.0 equiv.) to afford the porphyrin dimer **PDa** (Scheme 2) in 12 % yield. To further improve the synthetic efficiency, we investigated all of the factors that may influence the porphyrin dimer yield, including the reaction temperature, reaction time, solvent, and catalyst. Most of these factors did not have a positive impact on the yield; however, we found that the reaction solvent greatly influences the yields after the Chloranil oxidation, based on liquid chromatography-mass spectrometry (LCMS) analysis. Thus, we used the condensation reactions of bis(dipyrromethane), **3a** (1.0 equiv.) with dipyrromethane-dicarbinol, **4** (2.2 equiv.) as the model reaction for studying the influence of different solvent systems on the reaction yield. To obtain credible data, each experiment was repeated three times. We first examined several individual solvents, such as THF, CH_3CN, EtOAc, CH_2Cl_2, and $CHCl_3$, before investigating several mixed solvents.

Table 1 shows how the diverse solvent systems influenced the **PDa** synthesis with yields ranging from 17–25 % based on LCMS. The CH_2Cl_2/CH_3CN mixed-solvent (19 : 1) exhibited an especially positive effect on the reaction and gave the highest isolated yield, 18 %, which was an increase over previous results. Therefore, we supplemented the model reaction conditions using this solvent mixture. Thus, the optimised synthetic conditions using $InCl_3$ as catalyst were bis(dipyrromethane), **3**, to dipyrromethane-dicarbinol, **4**, ratio of 1 : 2.2 using CH_2Cl_2/CH_3CN (19 : 1) as the reaction solvent under an argon atmosphere for 30 min before oxidising the protoporphyrin with Chloranil (5.0 equiv.) in air for 6 h.

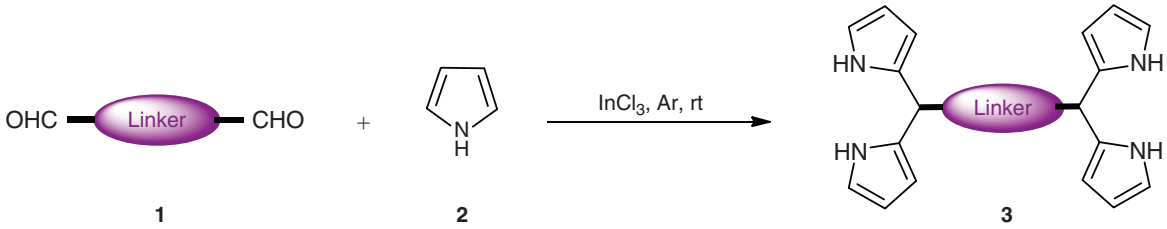
Based on the success of this protocol in preparing **PDa**, we used identical conditions to construct the other 12 porphyrin dimers shown in Scheme 2.

All nine types of linked bis(dipyrromethanes), **3**, readily formed the corresponding porphyrin dimers with yields ranging from 13 to 19 % (Table 2) in >95 % purity based on HPLC, which showed that this reaction model can be successfully exploited as a general and efficient protocol in the proper mixed-solvent.

The poor solubility of the reactants was efficiently improved by using the organic mixed-solvent, which included a sufficiency of CH_2Cl_2 and a small amount of CH_3CN. Introducing alkyloxy chains of appropriate length can improve the solubility of organic compounds in organic solvents, while chains that are too long will create strong stereo-hindrance rather than good solubility. As shown in Table 2, the porphyrin dimer yields were increased by lengthening the alkyloxy chain because the solubility of the bis(dipyrromethanes) and porphyrin dimers improved upon the introduction of alkyl chains with the appropriate length (**PDa**→**PDb**; **PDd**→**PDe**) but decreased due to the strong stereo-hindrance (**PDb**→**PDc**).

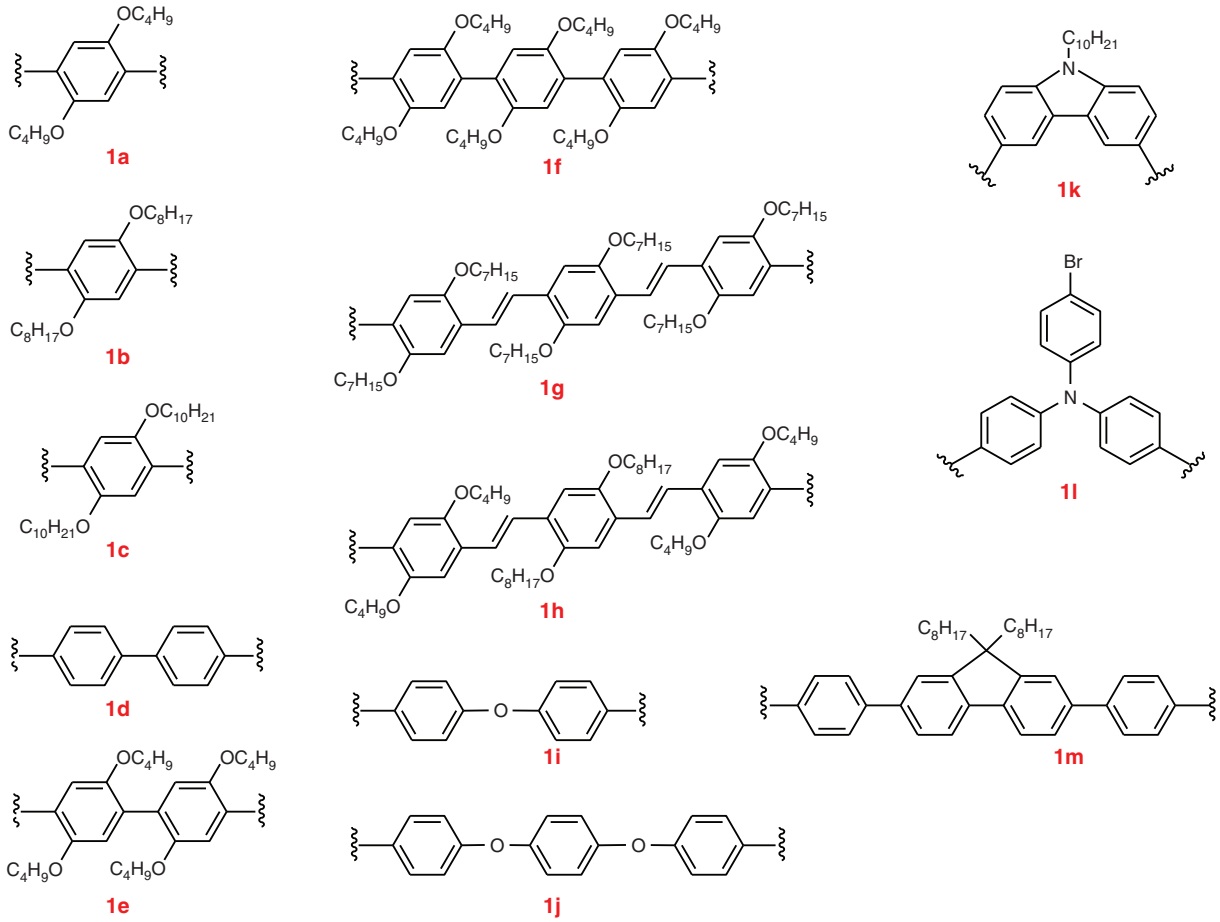
Absorption spectra of the porphyrin dimers were collected in CH_2Cl_2 (Table 3, Fig. 1, and Supplementary Material) for original photoelectric performance research.

The porphyrin dimers containing phenylene, biphenylene, triphenylene, triphenylenevinylene, diphenylether, 1,4-diphenoxybenzene, triphenylamine, carbazole, and diphenylfluorene linkers all exhibited four peaks characteristic of porphyrin, which confirmed the formation of these porphyrin dimers. All the obtained porphyrin dimers showed similar Soret bands at ~420 and 423 nm as well as visible bands at ~515, 550, 588, and 646 nm. Fig. 2 (we choose the **PDc** for example) shows that Soret bands of these porphyrin dimers were at 422 nm with a bathochromic shift (~2–4 nm) compared with tetraphenyl porphyrin (TPP) due to some of the phenyls being substituted with electron-rich or electron-deficient groups. The visible bands of these porphyrin dimers were identical with TPP except for **PDg** and **PDk** which have longer wavelengths of the IV bands due to the extra conjugation. However, we didn't see obvious shifts and splittings among the porphyrin dimers because of the various geometries and differing lengths of the linkers. This may be interpreted as the porphyrin moieties being the main chromophores in these molecules; the bridging groups extend the π-conjugation and reduce the electron cloud density in varying degrees, but this shows little effect on the porphyrin chromophores. On the other hand, from the spectra of absolute



1 2 3

Linker:



Scheme 1. Synthesis of bis(dipyrromethanes).

absorbance (see Supplementary Material), we can see that **PDd**, **PDe**, **PDg**, **PDi**, **PDj**, and **PDk**, showed stronger absorption at identical concentrations in a CH_2Cl_2 solution ($c = 1 \times 10^{-5}$ mol L^{-1}).

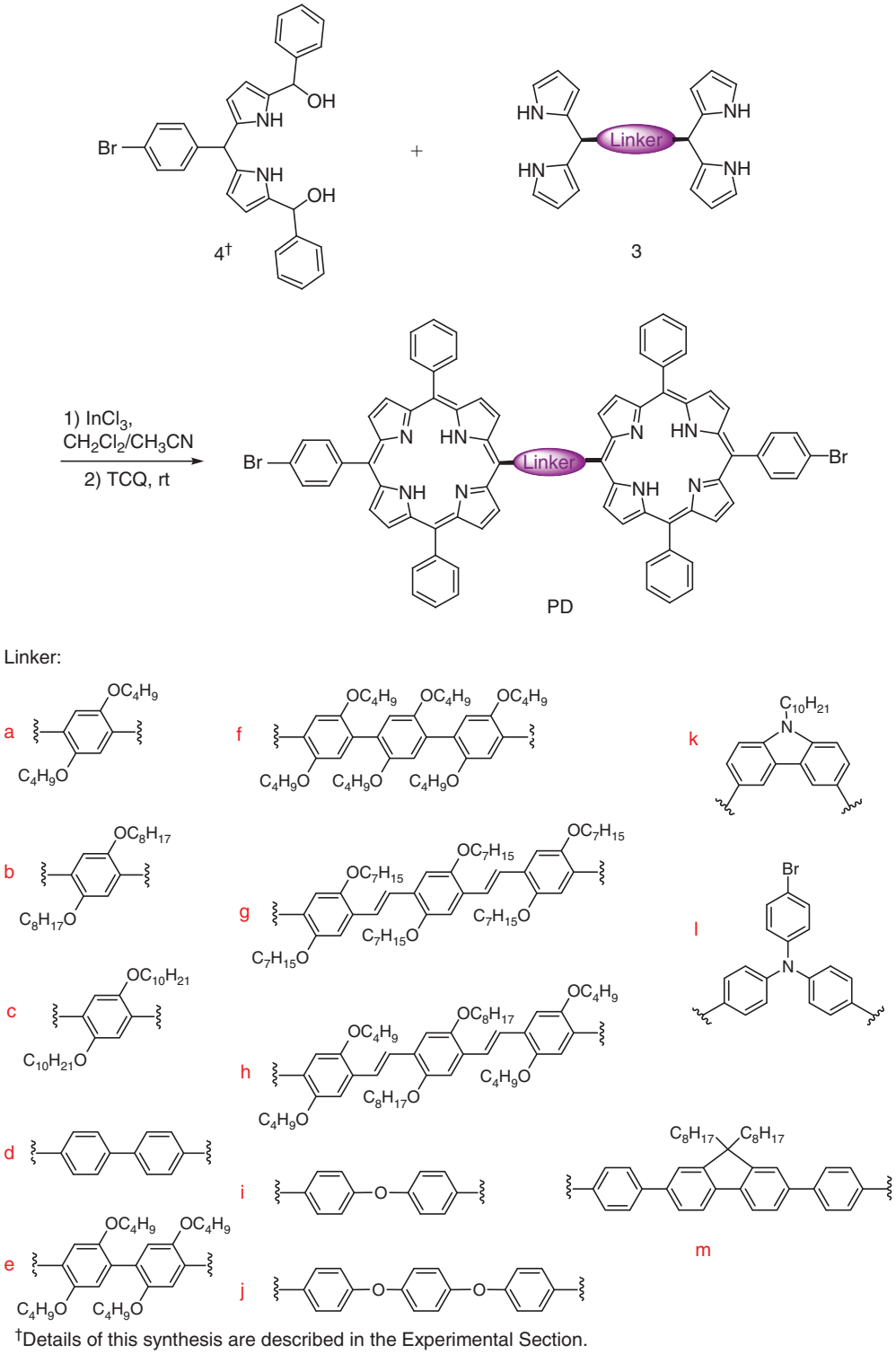
Conclusion

In summary, a series of novel porphyrin dimers containing phenylene, biphenylene, triphenylene, triphenylenevinylene, diphenylether, 1,4-diphenoxybenzene, triphenylamine, carbazole, and diphenylfluorene linkers were synthesised under mild conditions, at room temperature, through the simultaneous condensation-cyclisation-oxidation reaction of bis(dipyrromethanes) with dipyrromethane-dicarbinol, under catalysis by $InCl_3$ in a CH_2Cl_2 and CH_3CN mixed-solvent, with satisfactory yields ranging from 13 to 19 %. Such yields are acceptable for the one step synthesis of porphyrin dimers. By introducing alkyloxy chains and using a suitable organic mixed-solvent, we efficiently improved the poor solubility of the bis (dipyrromethanes) and porphyrin dimers. It is important to note that we successfully established a general route to afford a variety of bridging group-linked porphyrin dimers with desirable yields. This efficient protocol is applicable to constructing numerous types of porphyrin dimers with tunable, functional linkers. Furthermore, this protocol should extend to the single-step construction of longer functionalised multiporphyrin arrays. Further studies on the synthesis of more novel functionalised porphyrin dimers and even trimers based on this powerful route are in progress in our laboratory.

Experimental

General

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance (400 and 100 MHz, respectively). All melting points are uncorrected. The mass spectra were obtained via matrix-assisted laser desorption ionisation mass spectrometry (MALDI-MS) using an α-cyano-4-hydroxy-cinnamic acid (α-CHCA) matrix.



Scheme 2. Synthesis of porphyrin dimers.

Silica gel (40 µm average particle size) was used for column chromatography. Thin-layer chromatography was performed using SiliCycle silica gel 60 F_{254} TLC plates and visualised with ultraviolet light. All compounds were purchased from Alfa-Aesar and used without further purification unless otherwise noted. Pyrrole was distilled from CaH_2 before use. THF, CH_3OH and toluene were freshly distilled from CaH_2. **1g**,[11] **1j**,[16] 4,4′-oxydibenzaldehyde,[16] **1k**,[18] **3a**,[11] **3b**,[11] **3c**,[11] and **3d**[11] were synthesised according to the literature procedures and verified by ^{1}H NMR and MS. 4-Bromobenzaldehyde was commercially available.

Synthesis of Dialdehydes

*2,5,3′,6′-Tetrabutoxybiphenyl-4,4′-dicarbaldehyde (**1e**)*

A modified literature procedure was used for this reaction.[11] A mixture of 2,5-dibutoxy-4-formyl-1-(4,4,5,5-tetramethyl1,3,2-dioxaboralane-2-yl)benzene (3.76 g, 10 mmol),

Table 1. Solvents used for the construction of PDa

Entry	Solvent [v/v] (60 mL)	Temp	Time [h]	LCMS yield [%]	Isolated yield [%]
1	CH_2Cl_2	rt	0.5	19	12
2	$CHCl_3$	rt	0.5	19	13
3	CH_3CN	rt	0.5	19	13
4	EtOAc	rt	0.5	17	12
5	THF	rt	0.5	18	12
6	CH_2Cl_2/THF (9 : 1)	rt	0.5	19	14
7	CH_2Cl_2/EtOAc (9 : 1)	rt	0.5	19	13
8	CH_2Cl_2/CH_3CN (9 : 1)	rt	0.5	23	17
9	CH_2Cl_2/CH_3CN(14 : 1)	rt	0.5	25	18
10	CH_2Cl_2/CH_3CN(19 : 1)	rt	0.5	25	18
11	CH_2Cl_2/CH_3CN(24 : 1)	rt	0.5	23	17

Table 2. Yields for the porphyrin dimers under optimised conditions

Porphyrin dimers	LCMS yield [%]	Isolated yield [%]	Porphyrin dimers	LCMS yield [%]	Isolated yield [%]
PDa	26	18	**PDh**	22	16
PDb	26	19	**PDi**	25	18
PDc	25	18	**PDj**	26	18
PDd	24	17	**PDk**	23	14
PDe	25	18	**PDl**	23	13
PDf	26	18	**PDm**	22	14
PDg	23	16			

Table 3. Absorption spectral data of porphyrin dimers[A]

Cpd	Soret (V) ε [10^3 mol L^{-1} cm^{-1}]	Visible ε [10^3 mol L^{-1} cm^{-1}]			
		(IV)	(III)	(II)	(I)
TPP	418 (134)	515 (7)	550 (5)	589 (4)	645 (3)
PDa	420,423 (171)	514 (18)	548 (9)	587 (7)	645 (5)
PDb	420,422 (152)	515 (13)	551 (7)	588 (5)	645 (4)
PDc	420,422 (174)	516 (22)	551 (13)	589 (10)	647 (6)
PDd	421,423 (222)	516 (22)	552 (13)	590 (9)	646 (7)
PDe	417,423 (240)	516 (17)	551 (10)	589 (7)	646 (6)
PDf	423 (162)	516 (7)	552 (4)	590 (3)	645 (2)
PDg	426 (266)	525 (20)	562 (12)	600 (6)	657 (6)
PDh	421,423 (132)	515 (26)	552 (17)	588 (13)	647 (8)
PDi	421,423 (245)	515 (42)	550 (27)	589 (20)	646 (13)
PDj	418,423 (198)	514 (32)	550 (20)	588 (14)	646 (9)
PDk	423 (202)	524 (20)	561 (10)	603 (6)	660 (4)
PDl	419,422 (140)	517 (18)	555 (11)	592 (9)	648 (6)
PDm	423 (176)	516 (12)	552 (8)	590 (5)	646 (4)

[A]At room temperature in chloroform.

4-bromo-2,5-dibutoxybenzaldehyde (3.29 g, 10 mmol), $Pd(PPh_3)_4$ (0.58 g, 0.5 mmol), toluene (30 mL) and Na_2CO_3 solution (2 M, 30 mL) was heated to 85°C for 24 h under an argon atmosphere. The catalyst was removed via filtration, and the reaction mixture was washed with CH_2Cl_2 after cooling to room temperature. The organic layer was washed with saturated aqueous NH_4Cl (3×100 mL) and dried over anhydrous $MgSO_4$. After removing the solvent on a rotary evaporator, the crude product was purified by column chromatography using silica gel (CH_2Cl_2/petroleum ether = 1 : 1) to afford the title compound as a yellow solid (2.99 g, 60 %). M.p. 54–57°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.50 (s, 2H), 7.38 (s, 2H), 6.95 (s, 2H), 4.04 (t, $J = 6.3$ Hz, 4H), 3.92 (t, $J = 6.4$ Hz, 4H), 1.80 (m, 4H), 1.59 (m, 4H), 1.51 (m, 4H), 1.31 (m, 4H), 0.98 (t, $J = 7.3$ Hz, 6H), 0.86 (t, $J = 7.3$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.46, 155.75, 150.65, 135.17, 124.97, 116.74, 110.49, 69.24, 69.00, 31.45, 31.40, 19.42, 19.30, 13.88, 13.83; *m/z* (MALDI-TOF) 498.273; $[M+H]^+$ requires 498.298.

*2,5-Dibutoxy-1,4-bis[2,5-bis(butoxy)-4-formylphenyl] benzene (**1f**)*

A modified literature procedure was used for this reaction.[11] $Pd(PPh_3)_4$ (578 mg, 0.5 mmol) and Na_2CO_3 (30 mL, 2M in water) were added to a solution of 4-bromo-2,5-dibutoxybenzaldehyde (3.62 g, 11.0 mmol) and 2,5-dibutoxy-1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboralane-2-yl)benzene (2.37 g, 5.0 mmol) in toluene (30 mL), and the mixture was stirred under an argon atmosphere at 90°C for 24 h. After the reaction had cooled to room temperature, water (150 mL) was added to the flask, and the mixture was extracted with CH_2Cl_2 (3×100 mL). The organic phase was collected, washed with a saturated salt solution (3×80 mL), and dried over anhydrous $MgSO_4$. After concentrating on a rotary evaporator, the solution was purified by silica gel chromatography (eluting with petroleum ether/EtOAc = 30 : 1) to obtain the desired compound, **1f**, as a yellow solid (2.27 g, yield 61 %).M.p. 98–100°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.51 (s, 2H), 7.40 (s, 2H), 7.05 (s, 2H), 6.95 (s, 2H), 4.06 (t, $J = 6.3$ Hz, 4H), 3.95 (t, $J = 6.5$ Hz, 4H), 3.86 (t, $J = 6.5$ Hz, 4H), 1.81 (dd, $J = 14.3$, 6.7 Hz, 4H), 1.71–1.56 (m, 8H), 1.56–1.45 (m, 4H), 1.43–1.23 (m, 8H), 0.99 (t, $J =$ 7.4 Hz, 6H), 0.86 (dt, $J = 10.7$, 7.4 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.74, 156.01, 151.07, 150.14, 136.48, 127.70, 124.62, 117.46, 116.79, 110.72, 69.54, 69.30, 69.19, 31.80, 31.63, 31.60, 19.58, 19.47, 19.45, 14.04, 14.01, 14.00. *m/z* (MALDI-TOF) 718.445; $[M+H]^+$ requires 718.534.

*2,5-Bis(octyloxy)-1,4-bis[(2,5-bis(butoxy)-4-formyl) phenylenevinylene]benzene (**1h**)*

A modified literature procedure was used for this reaction.[11,15] A suspension of 2,5-bis(bromomethyl)-1,4-bis (octyloxy)benzene (2.86 g, 5.5 mmol) and triphenylphosphine (3.15 g, 12 mmol) in toluene (90 mL) was refluxed for 3 h. The solvent was then removed on a rotary evaporator. 2,5-Bis (butoxy)benzene-1,4-dialdehyde (2.76 g, 10 mmol) and CH_2Cl_2 (180 mL) were added to the flask followed by the dropwise addition of a lithium ethoxide solution (14 mL, 1.0 M in ethanol) via a syringe at room temperature over 10 min. The resulting solution was allowed to react for 30 min before pouring into dilute aqueous HCl. The organic layer was separated, washed with water, and dried over Na_2SO_4. The residue after solvent removal contained both the *E*- and *Z*-isomers. A solution of this isomer mixture and iodine (2 g, 7.8 mmol) in CH_2Cl_2 (90 mL) was stirred at room temperature overnight. The dark brown solution was then diluted with CH_2Cl_2 and washed with an aqueous $Na_2S_2O_3$ solution (1.0 M, 2×75 mL) and water. The organic phase was dried over Na_2SO_4. After concentrating on a rotary evaporator, the solution was loaded onto a silica gel column and eluted with a mixture of hexane and chloroform (1 : 1) to afford the title compound as a yellow fluorescent solid (4.12 g, 94 %). M.p. 150–151°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.45 (s, 2H), 7.56 (dd, 4H), 7.33 (s, 2H), 7.21 (s, 2H), 7.15 (s, 2H), 4.18–3.94 (m, 12H), 1.93–1.76 (m, 12H), 1.55 (t, 12H),

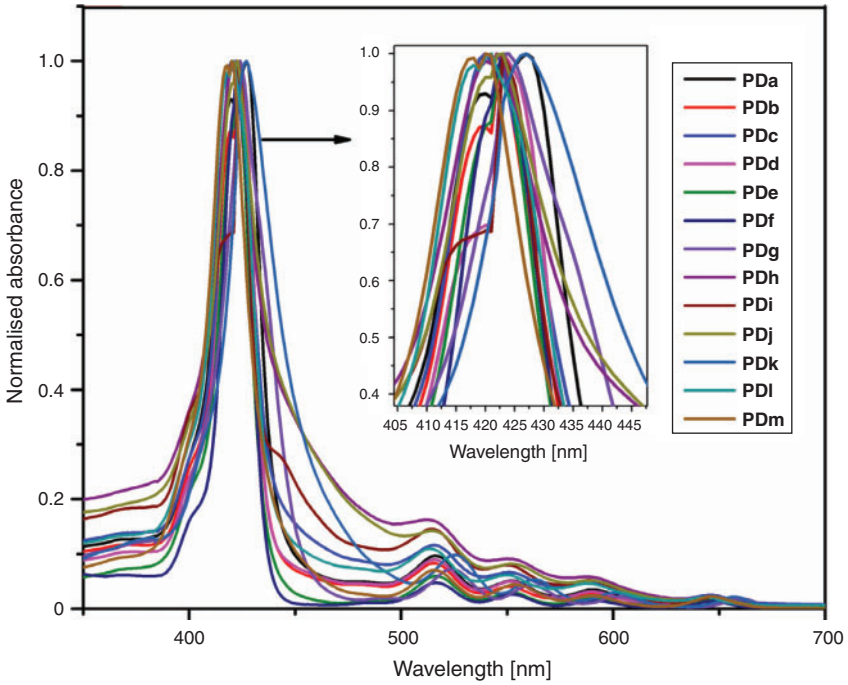


Fig. 1. Normalised absorption spectra of porphyrin dimers in CH_2Cl_2 solution ($c = 1 \times 10^{-5}$ mol L^{-1}).

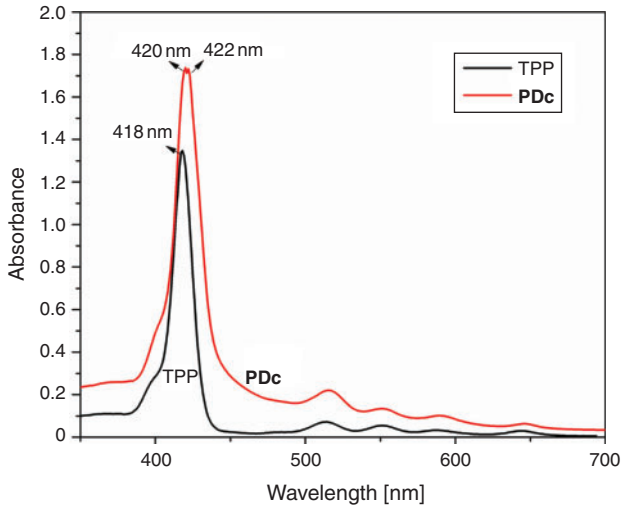


Fig. 2. Absorption spectra of TPP and **PDc** in a CH_2Cl_2 solution ($c = 1 \times 10^{-5}$ mol L^{-1}).

1.41–1.18 (m, 16H), 1.01 (td, 12H), 0.86 (d, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.18, 156.44, 151.55, 150.96, 135.16, 127.70, 127.11, 124.45, 123.45, 111.07, 110.73, 110.43, 69.63, 69.11, 69.03, 31.99, 31.53, 31.51, 29.64, 29.57, 29.46, 26.40, 22.78, 19.58, 19.50, 14.17, 14.05, 13.96; *m/z* (MALDI-TOF) 883.266; $[M+H]^+$ requires 883.245.

N,N-*Bis(4-formylphenyl)-4-bromophenylamine* (***1l***)

A modified literature procedure was used for this reaction.[17] $POCl_3$ (20 mL) was added dropwise to a solution of *N*,*N*-diphenyl-4-bromophenylamine (3.25 g, 10 mmol) in 1,2-dichloroethane (50 mL) and DMF (30 mL). The temperature was kept below 0°C using an ice salt bath and the resulting mixture was heated to 90°C for 48 h. After cooling to room temperature, the solution was poured into water (200 mL) and extracted with $CHCl_3$ (3 × 100 mL). The organic layer was separated, washed with water, dried over Na_2SO_4 and concentrated on a rotary evaporator. The residue was purified on a silica gel column (eluted with petroleum ether) and recrystallised (hexane) to give the desired compound, **1l**, as a green solid (2.47 g, yield 65 %). M.p. 205–207°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 2H), 7.79 (d, $J = 8.2$ Hz, 4H), 7.51 (d, $J = 8.3$ Hz, 2H), 7.19 (d, $J = 8.1$ Hz, 4H), 7.06 (d, $J = 8.2$ Hz, 2H).

2,7-*Bis(4-formylphenyl)-9,9-dioctylfluorene* (***1m***)

A modified literature procedure was used for this reaction.[19] A suspension of 2,7-dibromo-9,9-dioctylfluorene (1.65 g, 3 mmol), 4-formylphenyl boronic acid (0.93 g, 6.2 mmol), $Pd(PPh_3)_4$ (347 mg, 0.3 mmol), toluene (25 mL), and 2 M Na_2CO_3 solution (25 mL) was refluxed for 24 h under an argon atmosphere. The reaction mixture was filtered and washed with CH_2Cl_2 (50 mL) once it had cooled to room temperature. The separated organic layer was washed with saturated aqueous NH_4Cl (3 × 50 mL) and dried over $MgSO_4$. The solvent was removed on a rotary evaporator, and the crude residues was purified by column chromatography on silica gel (eluted with petroleum ether/EtOAc = 12 : 1) to give compound **1m** as a pale green solid (1.16 g, yield 65 %). M.p. 102–104°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 2H), 7.99 (d, $J = 8.0$ Hz, 4H), 7.84 (d, $J = 8.2$ Hz, 6H), 7.66 (d, $J = 7.9$ Hz, 2H), 7.62 (s, 2H), 2.14–1.99 (m, 4H), 1.22–0.98 (m, 20H), 0.87–0.72 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.75, 152.08, 147.54, 140.94, 138.93, 135.20, 130.26, 127.69, 126.53, 121.75, 120.49, 55.53, 40.29, 31.71, 29.89, 29.10, 23.80, 22.53, 13.96. *m/z* (MALDI-TOF) 598.381; $[M+H]^+$ requires 599.530.

Preparation of Bis(dipyrromethanes)

2,5,3′,6′-*Tetrabutoxy-4,4′-bis(dipyrromethan-5-yl) biphenyl* (***3e***)

Compound **1e** (645 mg, 1.29 mmol) was dissolved in dry pyrrole (20 mL, 289 mmol), and the solution was flushed with

argon for 10 min. $InCl_3$ (57 mg, 0.26 mmol) was added, and the reaction was allowed to proceed for 30 min. The reaction was quenched with NaOH powder (800 mg, 20 mmol). The mixture was stirred for 45 min and then filtered. Excess pyrrole was removed by distilling under reduced pressure, and the resulting yellow solid was treated with hexanes (10 mL). The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (eluted with hexane/CH_2Cl_2/ethyl acetate = 7 : 2 : 1) to give compound **3e** as a pale yellow solid (839 mg, 89 %). M.p. 108–111°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (brs, 4H), 6.90 (s, 2H), 6.78 (s, 2H), 6.68 (s, 4H), 6.14 (m, 4H), 5.97 (s, 4H), 5.71 (s, 2H), 3.82 (t, J = 6.3 Hz, 4H), 3.75 (t, J = 6.2 Hz, 4H), 1.63–1.46 (m, 8H), 1.29 (m, 8H), 0.86 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.87, 150.08, 132.83, 131.06, 117.45, 116.69, 116.65, 115.59, 108.37, 106.76, 69.55, 69.53, 39.34, 31.70, 31.68, 31.65, 19.38, 19.35, 19.30, 13.93; *m*/*z* (MALDI-TOF) 730.448; $[M+H]^+$ requires 730.446.

*2,5-Dibutoxy-1,4-bis[2,5-bis(butoxy)-4-(dipyrromethan-5-yl)phenyl]benzene (**3f**)*

Compound **1f** (1.8 g, 2.5 mmol) was dissolved in dry pyrrole (28 mL, 0.4 mol) and flushed with argon for 10 min. $InCl_3$ (111 mg, 0.5 mmol) was added, and the reaction was allowed to proceed for 30 min before quenching with NaOH powder (800 mg, 20 mmol). The mixture was stirred for 45 min and then filtered. Excess pyrrole was removed by distillation under reduced pressure, and the resulting yellow solid was treated with hexanes (10 mL). The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (eluted with hexane/CH_2Cl_2/ethyl acetate = 7 : 2 : 1) to give the compound **3f** as a pale yellow solid (2.1 g, yield 88 %). M.p. 174–177°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 4H), 6.98 (s, 2H), 6.95 (s, 2H), 6.80 (s, 2H), 6.69 (s, 4H), 6.15 (d, J = 2.3 Hz, 4H), 5.98 (s, 2H), 5.73 (s, 1H), 3.84 (t, J = 5.5 Hz, 8H), 3.77 (t, J = 6.2 Hz, 4H), 1.58 (dd, J = 18.3, 10.7 Hz, 12H), 1.33 (dd, J = 14.8, 7.5 Hz, 12H), 0.99–0.76 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.95, 150.07, 150.04, 132.80, 130.86, 127.80, 127.56, 117.57, 117.28, 116.59, 115.67, 108.29, 106.68, 69.50, 69.37, 39.30, 31.67, 31.64, 31.60, 19.31, 19.23, 13.83. *m*/*z* (MALDI-TOF) 950.592; $[M+H]^+$ requires 950.659.

*4,4′-Oxybis(phenyldipyrromethane) (**3i**)*

4,4′-Oxydibenzaldehyde (565 mg, 2.5 mmol) was dissolved in dry pyrrole (28 mL, 0.4 mol) and flushed with argon for 10 min. $InCl_3$ (111 mg, 0.5 mmol) was added, and the reaction was allowed to proceed for 30 min before quenching with powdered NaOH (0.8 g, 20 mmol). The mixture was stirred for 45 min and then filtered. Excess pyrrole was removed by distillation under reduced pressure and the resulting yellow solid was treated with hexanes (10 mL). The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (eluted with CH_2Cl_2) to afford a pale yellow solid (1.04 g, 91 %). M.p. 74–77°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (brs, 4H), 7.21–7.02 (m, 4H), 6.94 (t, J = 7.9 Hz, 4H), 6.70 (s, 4H), 6.16 (d, J = 2.6 Hz, 4H), 5.92 (s, 4H), 5.46 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.98, 137.06, 132.53, 129.59, 118.79, 117.25, 108.34, 107.18, 43.20; *m*/*z* (MALDI-TOF) 457.189; $[M+H]^+$ requires 458.210.

*1,4-Bis(4-dipyrromethylphenoxy)benzene (**3j**)*

Compound **1j** (550 mg, 1.73 mmol) was dissolved in dry pyrrole (20 mL, 0.30 mol) and flushed with argon for 10 min. $InCl_3$ (76 mg, 0.35 mmol) was added, and the reaction was allowed to proceed for 30 min before quenching with powdered NaOH (0.8 g, 20 mmol). The mixture was stirred for 45 min and then filtered. Excess pyrrole was removed by distillation under reduced pressure, and the resulting yellow solid was treated with hexanes (10 mL). The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (eluted with CH_2Cl_2) to afford a pale yellow solid (0.80 g, 84 %). M.p. 63–66°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (brs, 4H), 7.17 (d, J = 8.5 Hz, 4H), 6.98 (d, J = 4.3 Hz, 4H), 6.93 (d, J = 8.5 Hz, 4H), 6.71 (d, J = 1.2 Hz, 4H), 6.16 (d, J = 2.7 Hz, 4H), 5.92 (s, 4H), 5.46 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.59, 152.63, 136.82, 132.54, 129.59, 120.40, 118.22, 117.23, 108.37, 107.18, 43.22; *m*/*z* (MALDI-TOF) 549.229; $[M+H]^+$ requires 550.237.

*2,5-Bis(octyloxy)-1,4-bis{[(2,5-bis(butoxy)-4-(dipyrromethan-5-yl)]phenylenevinylene} benzene (**3h**)*

Compound **1h** (2.20 g, 2.5 mmol), pyrrole (28 mL, 0.4 mol), and $InCl_3$ (111 mg, 0.5 mmol) were reacted under an argon atmosphere at 50°C for 30 min. The reaction was quenched with powdered NaOH (0.8 g, 20 mmol) and stirring for 45 min before filtering. Excess pyrrole was removed by distillation under reduced pressure, and the resulting solid was treated with hexanes (20 mL). The solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (hexane/CH_2Cl_2/ethyl acetate = 4 : 2 : 1) to afford the title compound as a dark green solid (2.71 g, 97 %). M.p. 124–126°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.24 (brs, 4H), 7.43 (s, 4H), 7.16 (s, 2H), 7.13 (s, 2H), 6.72 (s, 2H), 6.68 (s, 4H), 6.14 (s, 4H), 5.95 (s, 4H), 5.71 (s, 2H), 4.03 (s, 4H), 3.90 (m, 8H), 1.78 (m, 8H), 1.61 (m, 16H), 1.33 (m, 16H), 1.06–0.80 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.25, 150.81, 132.61, 131.70, 127.66, 127.08, 123.66, 123.48, 116.74, 115.22, 111.30, 110.94, 108.47, 106.80, 69.74, 69.54, 69.50, 39.21, 32.01, 31.72, 29.72, 29.58, 29.45, 26.40, 22.79, 19.61, 19.36, 14.19, 14.09, 13.98; *m*/*z* (MALDI-TOF) 1114.730; $[M+H]^+$ requires 1114.749.

*2,5-Bis(octyloxy)-1,4-bis{[(2,5-bis(octyloxy)-4-(dipyrromethan-5-yl)]phenylenevinylene} benzene (**3g**)*

Compound **1 g** (1.02 g, 1.0 mmol), pyrrole (11.2 mL, 160 mmol), and $InCl_3$ (45 mg, 0.2 mmol) were reacted under an argon atmosphere at 50°C for 30 min. The reaction was quenched with powdered NaOH (0.4 g, 10 mmol) and stirring for 45 min before filtering. Excess pyrrole was removed by distillation under reduced pressure, and the resulting solid was treated with hexanes (20 mL). The solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (hexane/CH_2Cl_2/ethyl acetate = 4 : 2 : 1) to afford the title compound as a dark green solid (1.18 g, 94 %). M.p. 143–146°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.25 (s, 4H), 7.42 (s, 4H), 7.16 (s, 2H), 7.13 (s, 2H), 6.72 (s, 2H), 6.68 (s, 4H), 6.14 (d, J = 2.7 Hz, 4H), 5.95 (s, 4H), 5.70 (s, 2H), 4.03 (t, J = 6.2 Hz, 4H), 3.88 (dt, J = 16.2, 5.1 Hz, 8H), 1.91–1.69 (m, 12H), 1.68–1.42 (m, 12H), 1.29 (s, 36H), 0.87 (t, J = 7.1 Hz, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.34, 150.96, 150.79, 132.59, 131.67, 128.21, 127.12, 123.72, 123.52, 116.69, 115.21, 111.31, 110.98, 108.44, 106.76, 69.85, 69.76, 39.25, 31.97, 31.94, 29.72, 29.26, 29.24, 29.19, 26.35, 26.26, 26.11, 22.73,

22.71, 14.14. *m/z* (MALDI-TOF) 1254.805; $[M+H]^+$ requires 1254.806.

N-Decyl-3,6-bis(dipyrromethan-5-yl)carbazole (**3k**)

Compound **1k** (910 mg, 2.5 mmol), pyrrole (28 mL, 0.4 mol), and $InCl_3$ (111 mg, 0.5 mmol) were reacted under an argon atmosphere at 50°C for 30 min. The reaction was quenched with powdered NaOH (0.8 g, 20 mmol), and stirred for 45 min before filtering. Excess pyrrole was removed by distilling under reduced pressure, and the resulting solid was treated with hexanes (20 mL), which was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (hexane/CH_2Cl_2/ethyl acetate = 4 : 2 : 1) to afford the title compound as a yellow solid (1.32 g, 89 %). M.p. 109–111°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 4H), 7.82 (s, 2H), 7.31–7.25 (m, 4H), 6.67 (s, 4H), 6.16 (s, 4H), 5.95 (s, 4H), 5.60 (s, 2H), 4.24 (s, 2H), 1.82 (s, 2H), 1.23 (s, 14H), 0.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.23, 133.68, 133.02, 126.78, 123.02, 120.36, 117.39, 109.28, 108.67, 107.37, 44.27, 43.60, 32.16, 29.85, 29.80, 29.72, 29.57, 29.35, 27.63, 22.97, 14.42. *m/z* (MALDI-TOF) 595.368; $[M+H]^+$ requires 594.355.

N,N-Bis[4-(dipyrromethan-5-yl)phenyl]-4-bromophenylamine (**3l**)

Compound **1l** (951 mg, 2.5 mmol), pyrrole (28 mL, 0.4 mol), and $InCl_3$ (111 mg, 0.5 mmol) were reacted under an argon atmosphere at 50°C for 30 min. The reaction was quenched with powdered NaOH (0.8 g, 20 mmol) and stirred for 45 min before filtering. Excess pyrrole was removed by distillation under reduced pressure, and the resulting solid was treated with hexanes (20 mL), which was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (CH_2Cl_2/THF = 2 : 1) to afford the title compound as a yellow solid (1.4 g, 92 %). M.p. 137–140°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 4H), 7.31 (d, J = 8.3 Hz, 2H), 7.09 (d, J = 8.0 Hz, 4H), 6.99 (d, J = 7.7 Hz, 4H), 6.93 (d, J = 8.3 Hz, 2H), 6.72 (s, 4H), 6.17 (s, 4H), 5.93 (s, 4H), 5.43 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.74, 145.96, 136.95, 132.47, 132.13, 129.24, 125.04, 124.28, 117.21, 114.86, 108.40, 107.15, 43.37. *m/z* (MALDI-TOF) 611.169; $[M+H]^+$ requires 610.047.

2,7-Bis[4-(dipyrromethan-5-yl)phenyl]-9,9-dioctylfluorene (**3m**)

Compound **1m** (1.5 g, 2.5 mmol), pyrrole (28 mL, 0.4 mol), and $InCl_3$ (111 mg, 0.5 mmol) were reacted under an argon atmosphere at 50°C for 30 min. The reaction was quenched with powdered NaOH (0.8 g, 20 mmol), stirred for 45 min and filtered. Excess pyrrole was removed by distillation under reduced pressure, and the resulting solid was treated with hexanes (20 mL), which was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (hexane/CH_2Cl_2/ethyl acetate = 4 : 2 : 1) to afford the title compound **3m** as a yellow solid (2.0 g, 96 %). M.p. 121–125°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 4H), 7.76 (d, J = 7.7 Hz, 2H), 7.63 (d, J = 7.9 Hz, 4H), 7.60–7.50 (m, 4H), 7.33 (d, J = 7.8 Hz, 4H), 6.73 (s, 4H), 6.19 (d, J = 2.2 Hz, 4H), 5.99 (s, 4H), 5.55 (s, 2H), 2.08–1.96 (m, 4H), 1.27–0.99 (m, 20H), 0.80–0.71 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.90, 141.25, 140.53, 140.25, 139.75, 132.60, 128.98, 127.53, 126.08, 121.58, 120.16, 117.40, 108.72, 107.47, 55.44, 43.93, 40.56, 31.90, 30.17, 29.32, 24.01, 22.71, 14.15. *m/z* (MALDI-TOF) 830.529; $[M+H]^+$ requires 830.518.

Preparation of 5-(4-bromophenyl)dipyrromethane-1,9-diphenylcarbinol (**4**) (CAS: 744203–06–3)

A modified literature procedure was used for this reaction.[11] A solution of 5-(4-bromophenyl)dipyrromethane (3.01 g, 10 mmol) in dry toluene (150 mL) was treated with a EtMgBr solution (50 mL, 50 mmol, 1.0 M in THF) under argon at room temperature. After stirring for 60 min, a solution of C_6H_5COCl (3.5 mL, 30 mmol) in toluene (15 mL) was added over 15 min. After stirring for 3 h, the reaction was quenched with saturated aqueous NH_4Cl (80 mL). The solution was then extracted with ethyl acetate (2 × 40 mL). The organic phases were combined, washed with water, brine, and then dried over Na_2SO_4. After removing the toluene, the crude product was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2/ethyl acetate = 4 : 2 : 1) to afford the desired dipyrromethane-dicarbinol **4** as a brown solid. (1.63 g, 32 %). M.p. 114–116°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.36 (s, 2H), 7.74–7.78 (m, 4H), 7.45–7.52 (m, 4H), 7.38–7.45 (m, 6H), 6.58–6.59 (m, 2H), 5.98 (m, 2H), 5.65 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.64, 140.30, 139.41, 138.16, 131.92, 131.74, 131.17, 130.45, 129.43, 128.08, 121.46, 120.87, 111.19,44.32; *m/z* (MALDI-TOF) 509.00; $[M+H]^+$ requires 509.39.

General Procedure for the Efficient Synthesis of Novel Porphyrin Dimers via the Condensation Reaction of Various Bis(dipyrromethanes) and Dipyrromethanedicarbinol in the Presence of an $InCl_3$ Catalyst and Mixed-Solvent System

A sample of dipyrromethane-dicarbinol, **4** (crude, 1.1 mmol) was dissolved in CH_2Cl_2/CH_3CN (200 mL, 19 : 1) and before addition of bis(dipyrromethane) (0.5 mmol) under argon at room temperature. After a homogenous solution was obtained, $InCl_3$ (0.221 g, 1 mmol) was added and the reaction mixture was stirred at room temperature for 0.5 h. Chloranil (615 mg, 2.5 mmol) was then added and the reaction mixture was stirred for 6 h in air. The resulting mixture was passed through an alumina column (eluted with CH_2Cl_2) until the eluent was no longer dark. The collected eluent was then concentrated. The resulting crude product was purified by column chromatography on silica gel ($CHCl_3$/triethylamine = 100 : 1) and recrystallised from hexanes to afford a purple-black solid.

PDa

Following the general procedure, **3a** (255 mg, 0.5 mmol) and 5-(4-bromophenyl) dipyrromethane-1,9-diphenylcarbinol **4** (1.1 mmol) were reacted in CH_2Cl_2/CH_3CN (200 mL, 19 : 1) under an argon atmosphere at room temperature. The intermediate was oxidised by Chloranil (615 mg, 2.5 mmol) in air. The **PDa** yield was 26 % based on LCMS. The resulting product was purified by column chromatography on silica gel ($CHCl_3$/triethylamine = 100 : 1), and recrystallised from hexane to afford a purple-black solid. (131 mg, 18 %). M.p. >280°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (s, 4H), 9.03 (s, 4H), 8.85–8.91 (s, 8H), 8.09–8.30 (m, 12H), 8.06 (s, 2H), 7.81–7.93 (m, 16H), 3.87–3.90 (t, 4H), 0.85–0.98 (s, 4H), 0.39–0.44 (d, 4H), 0.20–0.22 (t, 6H), −2.62 (s, 4H). *m/z* (MALDI-TOF) 1453.408; $[M+H]^+$ requires 1453.365; UV-Vis ($CHCl_3$) λ_{max}: 420, 423(Soret), 514, 548, 587, 645 nm.

PDb

Following the general procedure, **3b** (312 mg, 0.5 mmol) and 5-(4-bromophenyl) dipyrromethane-1,9-diphenylcarbinol **4**

(1.1 mmol) were reacted in CH_2Cl_2/CH_3CN (200 mL, 19 : 1) under an argon atmosphere at room temperature. The intermediate was oxidised by Chloranil (615 mg, 2.5 mmol) in air. The **PDb** yield was 26 % based on LCMS. The resulting product was purified by column chromatography on silica gel ($CHCl_3$/triethylamine = 100 : 1) and recrystallised from hexane to afford a purple-black solid. (149 mg, 19 %). M.p. 146–150°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (s, 4H), 9.03 (s, 4H), 8.86 (m, 8H), 8.32–8.05 (m, 14H), 8.92–7.77 (m, 16H), 3.88 (s, 4H), 0.98 (s, 4H), 0.91–0.77 (m, 4H), 0.66 (m, 4H), 0.58–0.26 (m, 18H), −2.63 (s, 4H). *m*/*z* (MALDI-TOF) 1566.240; $[M+H]^+$ requires 1565.576; UV-Vis ($CHCl_3$) λ_{max}: 420, 422 (Soret), 515, 551, 588, 645 nm.

PDc

Following the general procedure, **3c** (339 mg, 0.5 mmol) and 5-(4-bromophenyl) dipyrromethane-1,9-diphenylcarbinol **4** (1.1 mmol) were reacted in CH_2Cl_2/CH_3CN (200 mL, 19 : 1) under argon an atmosphere at room temperature. The intermediate was oxidised by Chloranil (615 mg, 2.5 mmol) in air. The **PDc** yield was 25 % based on LCMS. The resulting product was purified by column chromatography on silica gel ($CHCl_3$/triethylamine = 100 : 1) and recrystallised from hexane to afford a purple-black solid (146 mg, 18 %). M.p. 195–198°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (s, 4H), 9.03 (s, 4H), 8.86 (m, 8H), 8.32–8.05 (m, 14H), 8.92–7.77 (m, 16H), 3.88 (s, 4H), 0.98 (s, 4H), 0.91–0.77 (m, 4H), 0.66 (m, 4H), 0.58–0.26 (m, 26H), −2.63 (s, 4H). *m*/*z* (MALDI-TOF) 1621.573; $[M+H]^+$ requires 1621.682; UV-Vis ($CHCl_3$) λ_{max}: 420, 422 (Soret), 516, 551, 589, 647 nm.

PDd

Following the general procedure, **3d** (221 mg, 0.5 mmol) and 5-(4-bromophenyl) dipyrromethane-1,9-diphenylcarbinol **4** (1.1 mmol) were reacted in CH_2Cl_2/CH_3CN (200 mL, 19 : 1) under an argon atmosphere at room temperature. The intermediate was oxidised by Chloranil (615 mg, 2.5 mmol) in air. The **PDd** yield was 24 % based on LCMS. The resulting product was purified by column chromatography on silica gel ($CHCl_3$/triethylamine = 100 : 1) and recrystallised from hexane to afford a purple-black solid (118 mg, 17 %). M.p. >280°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (s, 4H), 8.85–8.90 (s, 12H), 8.42 (s, 4H), 8.26 (t, 8H), 8.08–8.14 (s, 4H), 7.92 (s, 4H), 7.71–7.83 (s, 16H), −2.73 (s, 4H); *m*/*z* (MALDI-TOF) 1385.228; $[M+H]^+$ requires 1385.247; UV-Vis ($CHCl_3$) λ_{max}: 421, 423 (Soret), 516, 552, 590, 646 nm.

PDe

Following the general procedure, **3e** (365 mg, 0.5 mmol) and 5-(4-bromophenyl) dipyrromethane-1,9-diphenylcarbinol **4** (1.1 mmol) were reacted in CH_2Cl_2/CH_3CN (200 mL, 19 : 1) under an argon atmosphere at room temperature. The intermediate was oxidised by Chloranil (615 mg, 2.5 mmol) in air. The **PDe** yield was 25 % based on LCMS. The resulting product was purified by column chromatography on silica gel ($CHCl_3$/triethylamine = 100 : 1) and recrystallised from hexane to afford a purple-black solid (151 mg, 18 %). M.p. 193–197°C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 9.09 (d, J = 3.8 Hz, 4H), 8.98–8.78 (m, 12H), 8.26 (s, 8H), 8.12 (m, 4H), 7.92 (s, 4H), 7.71–7.81 (m, 16H), 4.16 (t, J = 5.8 Hz, 4H), 3.99 (t, J = 5.9 Hz, 4H), 1.94–1.79 (m, 4H), 1.66–1.53 (m, 4H), 0.77–1.05 (m, 10H), 0.57 (dd, J = 14.6, 7.3 Hz, 4H), 0.29 (t, J = 7.2 Hz, 6H), −2.69 (s, 4H); *m*/*z* (MALDI-TOF) 1673.515; $[M+H]^+$ requires 1673.671; UV-Vis ($CHCl_3$) λ_{max}: 417, 423 (Soret), 516, 551, 589, 646 nm.

PDf

Following the general procedure, **3f** (475 mg, 0.5 mmol) and 5-(4-bromophenyl) dipyrromethane-1,9-diphenylcarbinol **4** (1.1 mmol) were reacted in CH_2Cl_2/CH_3CN (200 mL, 19 : 1) under an argon atmosphere at room temperature. The intermediate was oxidised by Chloranil (615 mg, 2.5 mmol) in air. The **PDf** yield was 26 % based on LCMS. The resulting product was purified by column chromatography on silica gel ($CHCl_3$/triethylamine = 100 : 1) and recrystallised from hexane to afford a purple-black solid (175 mg, 18 %). M.p. >300°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (d, J = 4.5 Hz, 4H), 8.87 (d, J = 4.7 Hz, 8H), 8.83 (d, J = 4.5 Hz, 4H), 8.24 (s, 8H), 8.11 (dd, J = 20.5, 7.5 Hz, 4H), 7.91 (d, J = 6.3 Hz, 4H), 7.85–7.71 (m, 12H), 7.49 (d, J = 3.5 Hz, 6H), 4.24 (t, J = 6.3 Hz, 4H), 4.04 (t, J = 6.4 Hz, 4H), 3.87 (t, J = 6.3 Hz, 4H), 1.90 (dd, J = 14.0, 6.5 Hz, 4H), 1.73 (dd, J = 14.2, 6.7 Hz, 4H), 1.64 (dd, J = 14.8, 7.4 Hz, 4H), 1.42 (dd, J = 14.8, 7.4 Hz, 4H), 1.09 (t, J = 7.4 Hz, 6H), 1.01 (dd, J = 14.0, 7.1 Hz, 4H), 0.89 (t, J = 7.3 Hz, 6H), 0.53 (dd, J = 14.8, 7.4 Hz, 4H), 0.25 (t, J = 7.3 Hz, 6H), −2.71 (s, 4H); *m*/*z* (MALDI-TOF) 1893.667; $[M+H]^+$ requires 1893.676; UV-Vis ($CHCl_3$) λ_{max}: 423 (Soret), 516, 552, 590, 645 nm.

PDg

Following the general procedure, **3 g** (628 mg, 0.5 mmol) and 5-(4-bromophenyl) dipyrromethane-1,9-diphenylcarbinol **4** (1.1 mmol) were reacted in CH_2Cl_2/CH_3CN (200 mL, 19 : 1) under an argon atmosphere at room temperature. The intermediate was oxidised by Chloranil (615 mg, 2.5 mmol) in air. The **PDg** yield was 23 % based on LCMS. The resulting product was purified by column chromatography on silica gel ($CHCl_3$/triethylamine = 100 : 1) and recrystallised from hexane to afford a purple-black solid (176 mg, 16 %). M.p. 208–211°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, J = 1.9 Hz, 4H), 8.84 (d, J = 12.9 Hz, 12H), 8.23 (dd, J = 17.0, 4.6 Hz, 8H), 8.10 (dd, J = 24.0, 6.9 Hz, 4H), 7.88 (d, J = 18.2 Hz, 8H), 7.78 (s, 12H), 7.64 (s, 4H), 7.40 (s, 2H), 4.23 (s, 4H), 4.09 (s, 4H), 3.88 (s, 4H), 2.01 (s, 4H), 1.91 (s, 4H), 1.66 (s, 4H), 1.36 (s, 12H), 1.26 (s, 18H), 0.97 (s, 4H), 0.87 (d, J = 21.5 Hz, 12H), 0.52 (dd, J = 35.4, 6.3 Hz, 8H), 0.32 (d, J = 7.0 Hz, 12H), −2.75 (s, 4H); *m*/*z* (MALDI-TOF) 2198.987; $[M+H]^+$ requires 2198.531; UV-Vis ($CHCl_3$) λ_{max}: 426 (Soret), 525, 562, 600, 657 nm.

PDh

Following the general procedure, **3h** (558 mg, 0.5 mmol) and 5-(4-bromophenyl) dipyrromethane-1,9-diphenylcarbinol **4** (1.1 mmol) were reacted in CH_2Cl_2/CH_3CN (200 mL, 19 : 1) under an argon atmosphere at room temperature. The intermediate was oxidised by Chloranil (615 mg, 2.5 mmol) in air. The **PDh** yield was 22 % based on LCMS. The resulting product was purified by column chromatography on silica gel ($CHCl_3$/triethylamine = 100 : 1) and recrystallised from hexane to afford a purple-black solid (165 mg, 16 %). M.p. 217–220°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 4H), 8.85 (s, 12H), 8.22 (s, 8H), 8.08 (s, 4H), 7.78 (s, 12H), 7.64 (s, 4H), 7.41 (s, 2H), 3.88–4.23 (m, 12H), 1.91–2.01(m, 8H), 1.26–1.66 (m, 18H), 0.87–0.97 (m, 12H), 0.52 (m, 8H), 0.32 (d, J = 7.0 Hz, 12H), −2.75 (s, 4H); *m*/*z* (MALDI-TOF) 2058.185; $[M+H]^+$ requires 2058.265; UV-Vis ($CHCl_3$) λ_{max}: 421, 423 (Soret), 515, 552, 588, 647 nm.

PDi

Following the general procedure, the reaction was conducted with **3i** (229 mg, 0.5 mmol) and 5-(4-bromophenyl)dipyrromethane-1,9-diphenylcarbinol **4** (1.1 mmol) in CH_2Cl_2/ CH_3CN (200 mL, 19 : 1) under argon atmosphere at room temperature. The formed intermediate was oxidised with Chloranil (615 mg, 2.5 mmol) in the air. The yield of **PDi** was 25 % on LCMS. The resulting product was purified by column chromatography on silica gel ($CHCl_3$/triethylamine = 100 : 1), and was recrystallised from hexane to afford a purple-black solid (126 mg, 18 %). M.p. 218–222°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (s, 4H), 8.80–8.90 (m, 12H), 8.34 (m, 4H), 8.09–8.22 (m, 12H), 7.90 (m, 6H), 7.78 (s, 8H), 7.44 (s, 8H), −2.79 (s, 4H); *m*/*z* (MALDI-TOF) 1401.263; $[M+H]^+$ requires 1401.247; UV-Vis ($CHCl_3$) λ_{max}: 421, 423 (Soret), 515, 550, 589, 646 nm.

PDj

Following the general procedure, **3j** (275 mg, 0.5 mmol) and 5-(4-bromophenyl) dipyrromethane-1,9-diphenylcarbinol **4** (1.1 mmol) were reacted in CH_2Cl_2/CH_3CN (200 mL, 19 : 1) under an argon atmosphere at room temperature. The intermediate was oxidised by Chloranil (615 mg, 2.5 mmol) in air. The **PDj** yield was 26 % based on LCMS. The resulting product was purified by column chromatography on silica gel ($CHCl_3$/ triethylamine = 100 : 1) and recrystallised from hexane to afford a purple-black solid (134 mg, 18 %). M.p. >280°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (s, 4H), 8.83–8.87 (m, 12H), 8.21 (s, 8H), 8.09 (m, 4H), 7.78–7.90 (s, 16H), 7.66 (s, 4H), 7.49 (s, 8H), −2.78 (s, 4H); *m*/*z* (MALDI-TOF) 1493.213; $[M+H]^+$ requires 1493.242; UV-Vis ($CHCl_3$) λ_{max}: 418, 423 (Soret), 514, 550, 588, 646 nm.

PDk

Following the general procedure, **3k** (297 mg, 0.5 mmol) and 5-(4-bromophenyl) dipyrromethane-1,9-diphenylcarbinol **4** (1.1 mmol) were reacted in CH_2Cl_2/CH_3CN (200 mL, 19 : 1) under an argon atmosphere at room temperature. The intermediate was oxidised by Chloranil (615 mg, 2.5 mmol) in air. The **PDk** yield was 23 % based on LCMS. The resulting product was purified by column chromatography on silica gel ($CHCl_3$/ triethylamine = 100 : 1) and recrystallised from hexane to afford a purple-black solid (108 mg, 14 %). M.p. >300°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, J = 18.5 Hz, 4H), 8.79 (d, J = 14.6 Hz, 12H), 8.45 (d, J = 7.5 Hz, 2H), 8.28–8.11 (m, 8H), 8.06 (dd, J = 14.5, 7.8 Hz, 4H), 7.98–7.81 (m, 6H), 7.82–7.65 (m, 12H), 4.82 (s, 2H), 2.37 (s, 2H), 1.80 (s, 2H), 1.39–1.33 (m, 12H), 0.88 (t, J = 8.1 Hz, 3H), −2.82 (s, 4H); *m*/*z* (MALDI-TOF) 1539.460; $[M+H]^+$ requires 1538.452; UV-Vis ($CHCl_3$) λ_{max}: 423 (Soret), 524, 561, 603, 660 nm.

PDl

Following the general procedure, **3l** (305 mg, 0.5 mmol) and 5-(4-bromophenyl) dipyrromethane-1,9-diphenylcarbinol **4** (1.1 mmol) were reacted in CH_2Cl_2/CH_3CN (200 mL, 19 : 1) under an argon atmosphere at room temperature. The intermediate was oxidised by Chloranil (615 mg, 2.5 mmol) in air. The **PDl** yield was 23 % based on LCMS. The resulting product was purified by column chromatography on silica gel ($CHCl_3$/ triethylamine = 100 : 1) and was recrystallised from hexane to afford a purple-black solid (101 mg, 13 %). M.p. >300°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (s, 4H), 8.97–8.79 (m, 12H), 8.25 (t, J = 7.8 Hz, 12H), 8.10 (d, J = 7.7 Hz, 4H), 7.90 (d, J = 7.6 Hz, 4H), 7.77 (d, J = 6.4 Hz, 16H), 7.67 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.3 Hz, 2H), −2.76 (s, 4H); *m*/*z* (MALDI-TOF) 1555.274; $[M+H]^+$ requires 1555.254; UV-Vis ($CHCl_3$) λ_{max}: 419, 422 (Soret), 517, 555, 592, 648 nm.

PDm

Following the general procedure, **3m** (415 mg, 0.5 mmol) and 5-(4-bromophenyl) dipyrromethane-1,9-diphenylcarbinol **4** (1.1 mmol) were reacted in CH_2Cl_2/CH_3CN (200 mL, 19 : 1) under an argon atmosphere at room temperature. The intermediate was oxidised by Chloranil (615 mg, 2.5 mmol) in air. The **PDm** yield was 22 % based on LCMS. The resulting product was purified by column chromatography on silica gel ($CHCl_3$/ triethylamine = 100 : 1) and recrystallised from hexane to afford a purple-black solid (116 mg, 14 %). M.p. >300°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (d, J = 4.5 Hz, 4H), 8.94–8.86 (m, 8H), 8.84 (d, J = 4.4 Hz, 4H), 8.36 (d, J = 7.8 Hz, 4H), 8.24 (d, J = 6.1 Hz, 8H), 8.13 (dd, J = 15.3, 8.0 Hz, 8H), 8.05–7.97 (m, 6H), 7.91 (d, J = 8.0 Hz, 4H), 7.79 (d, J = 7.1 Hz, 12H), 2.35–2.24 (m, 4H), 1.00–0.86 (m, 24H), 0.83 (t, J = 7.3 Hz, 6H), −2.75 (s, 4H); *m*/*z* (MALDI-TOF) 1662.347; $[M+H]^+$ requires 1662.347; UV-Vis ($CHCl_3$) λ_{max}: 423 (Soret), 516, 552, 590, 646 nm.

Supplementary Material

^{1}H-, ^{13}C NMR spectra for all unknown compounds and UV-Vis spectra for all porphyrin dimers are available on the Journal's website.

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