DOI: 10.1002/adsc.201000336

Efficient Synthesis of Novel Bis(dipyrromethanes) with Versatile Linkers *via* Indium(III) Chloride-Catalyzed Condensation of Pyrrole and Dialdehydes

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Received: April 30, 2010; Revised: September 28, 2010; Published online: November 17, 2010

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201000336.

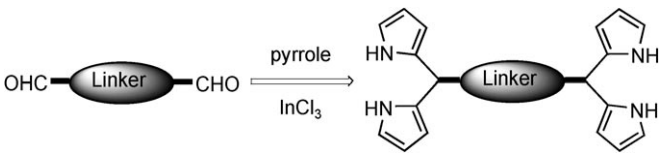
Abstract: A new efficient and mild protocol for synthesizing a series of novel bis(dipyrromethanes) with versatile arylene linkers through an indium(III) chloride-catalyzed condensation reaction between various dialdehydes and pyrrole has been developed. This protocol is applicable to constructing a variety of bis(dipyrromethanes) with diverse functional linkers, which provides a powerful route to construct libraries of functionalized porphyrin dimers and even multiporphyrin arrays.

Keywords: bis(dipyrromethanes); dialdehydes; indium(III) chloride-catalyzed condensation; pyrroles

The organization of multiple porphyrins into arrays has provided the basis for a variety of functional molecular architectures.[1–4] The research into the design and synthesis of novel multiporphyrin arrays has attracted much attention. The common method for constructing multiporphyrin arrays is coupling intact porphyrin building blocks;[5] however, this inconvenient stepwise approach only introduces fixed linkers among the porphyrin units, which seriously limits the possible diversity and functionality of the multiporphyrin arrays. The condensation of bis(dipyrromethanes) by the "2+2" method is a potentially important strategy for the design and synthesis of novel multiporphyrin arrays,[6] since the tunability of linkers in bis(dipyrromethanes) offers more opportunities to construct multiporphyrin arrays with targeted functions. Thus, the key procedure in this strategy is how to obtain the vital intermediate compounds – bis(dipyrromethanes), especially those containing versatile functionalized linkers.

The basic idea of making bis(dipyrromethanes) from a diformyl compound was demonstrated first by Chang in the 1980s and exploited by Sessler, McLendon, Osuka, Lindsey and others.[7] Most of the reported bis(dipyrromethanes) were utilized to synthesize diporphyrins *via* condensation of each bis(dipyrromethane) with two dipyrromethane units. Nevertheless, to the best of our knowledge, except these abovementioned diporphyrins, multiporphyrin arrays with more porphyrin units have not yet been obtained through condensation reactions of bis(dipyrromethanes), without coupling intact porphyrin building blocks.

Herein, we report a general and efficient protocol to synthesize a series of novel bis(dipyrromethanes) containing various arylene linkers *via* $InCl_3$-catalyzed condensation of functionalized dialdehydes and pyrrole (Scheme 1). We also obtained new diporphyrins using these novel bis(dipyrromethanes) for cyclization with dipyrromethanes under mild conditions. This method could be applied to constructing novel multiporphyrin arrays that contain numerous porphyrin units. These multiporphyrin arrays could be synthesized through simultaneous condensation–cyclization–polymerization of different or the same bis(dipyrro-

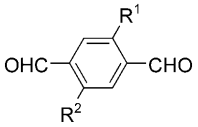


Scheme 1. Synthesis of bis(dipyrromethanes) containing versatile linkers.

methane) monomers, and the polymerization reaction could be terminated by dipyrromethanes. It should be noted that by this method, multiporphyrin arrays with more porphyrin units bearing versatile linkers could be prepared just by one step. Thus, a series of functionalized multiporphyrin arrays could be obtained by this one-step method easily and this offers us a good chance to further study the properties of multiporphyrin compounds. Our work will significantly extend and enrich porphyrin chemistry.

With the ultimate objective of constructing a series of novel multiporphyrin arrays, a series of phenylene-linked, biphenylene-linked, triphenylene-linked, and triphenylenevinylene-linked dialdehydes with various functional groups has been prepared. Firstly, as can be seen from Table 1, both electron-deficient and electron-rich functional groups (entries 2–6) can be smoothly incorporated into phenylene-linked dialdehydes according to literature procedures or with some modifications, e.g., compounds **2**,[8] **3**,[8] and **6**;[9] procedures for the synthesis of compounds **4** and **5** are given in the Experimental Section and Supporting Information, respectively.

Table 1. Phenylene-linked dialdehydes.



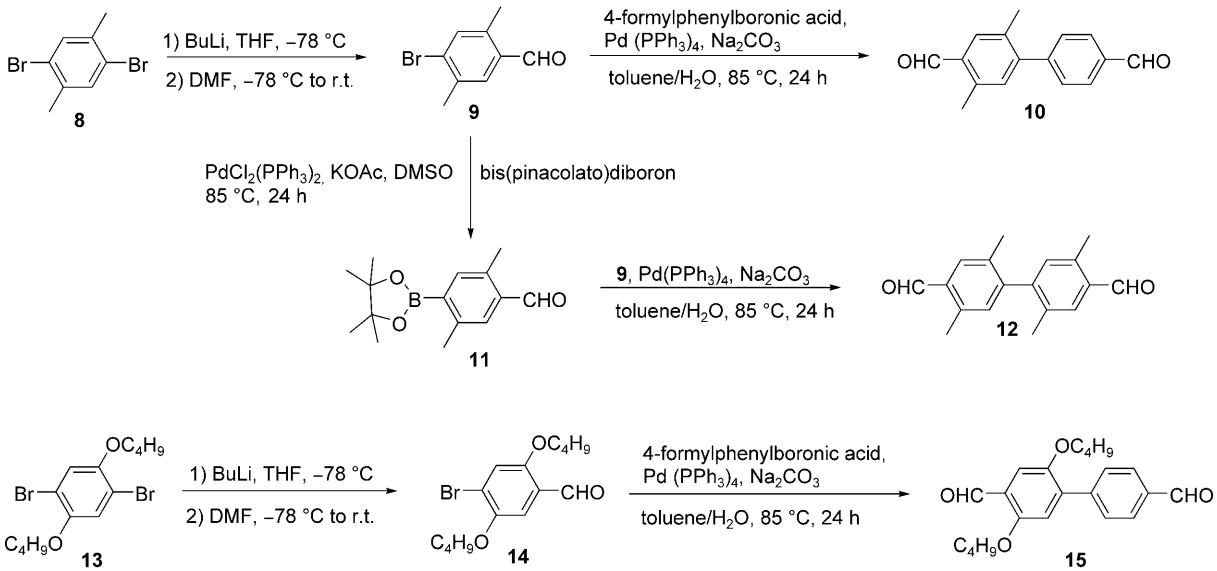
Entry	Dialdehyde	R^1	R^2
1	**1**[a]	H	H
2	**2**	Br	H
3	**3**	Br	Br
4	**4**	OC_4H_9	OC_4H_9
5	**5**	OC_7H_{15}	OC_7H_{15}
6	**6**	$OC_{10}H_{21}$	$OC_{10}H_{21}$

[a] Compound **1** was commercially available.

Furthermore, biphenylene-linked dialdehydes were prepared by using Suzuki–Miyaura coupling as the key reaction (Scheme 2). Starting with compound **8**,[8b] we performed a Br/Li-exchange with *n*-BuLi followed by reaction with DMF affording aldehyde **9**,[10] and aldehyde **14** was gained by the same method by using compound **13**[11] as starting material. Subsequently, cross-coupling of **9** (or **14**) and 4-formylphenylboronic acid gave the dialdehyde **10** (or **15**).[12] Boronate **11** was prepared from **9** by modified Miyaura coupling with bis(pinacolato)diboron.[13] Finally, cross-coupling of **11** and **9** gave the corresponding **12** (see Supporting Information).

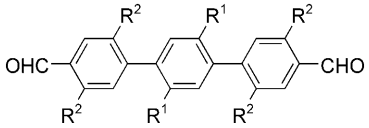
The terphenylene-linked dialdehydes were synthesized *via* an analogous procedure (Table 2). Suzuki bis-coupling of either **8** or 1,4-dibromo-2,5-bis-(decyloxy)benzene[14] with 4-formylphenylboronic acid afforded either the dialdehyde **16** or **18** in good yields (75% and 67%, respectively).[12] Dialdehyde **17** was prepared by bis-coupling of **9** with 1,4-diboronate derived from **8** *via* Miyaura cross-coupling reaction (see Supporting Information).

Three triphenylenevinylene-linked dialdehydes were also prepared during our experiments (Table 3). Compound **21** was produced according to the published procedure.[9] Firstly, 2,5-bis(bromomethyl)-1,4-bis(decyloxy)benzene was converted to a diphosphonium salt, and then a double Wittig reaction with dialdehyde **1**, **4** or **6** gave the corresponding triphenylenevinylene-linked dialdehyde **19**, **20** or **21** in high yields of 87%, 82% and 84%, respectively.



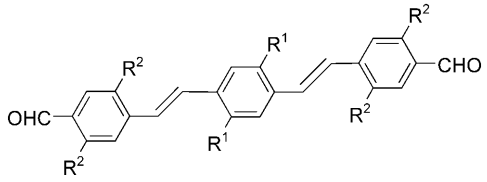
Scheme 2. Synthesis of biphenylene-linked dialdehydes.

Table 2. Terphenylene-linked dialdehydes.



Entry	Dialdehyde	R^1	R^2
1	**16**	CH_3	H
2	**17**	CH_3	CH_3
3	**18**	$OC_{10}H_{21}$	H

Table 3. Triphenylenevinylene-linked dialdehydes.



Entry	Dialdehyde	R^1	R^2
1	**19**	$OC_{10}H_{21}$	H
2	**20**	$OC_{10}H_{21}$	OC_4H_9
3	**21**	$OC_{10}H_{21}$	$OC_{10}H_{21}$

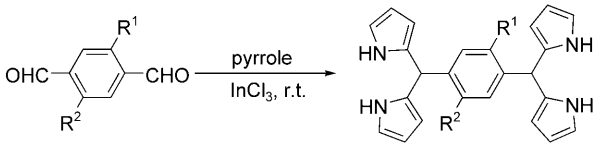
With these libraries of dialdehydes in hand, our attention shifted to the synthesis of the corresponding bis(dipyrromethanes).

We extend the strategy of synthesizing dipyrromethanes to the preparation of bis(dipyrromethanes).[7e,15] All of the bis(dipyrromethanes) reported in this paper were synthesized efficiently under identified conditions *via* condensation of arylene-linked dialdehydes and pyrrole. The following are the details for the reaction conditions: under argon; a 150:1 ratio of pyrrole:dialdehyde; 0.1 equivalent of $InCl_3$ as catalyst; at room temperature for 2 h. All reported yields were based on the weight of the isolated bis(dipyrromethanes) and the purity was measured by HLPC.

Firstly, this method was applied to the synthesis of a range of phenylene-linked bis(dipyrromethanes) bearing various functional groups in the phenyl rings. As shown in Table 4, the condensation reaction occurred smoothly for both electron-deficient (**2**, **3**) and electron-rich (**4**, **5**, **6**) substrates, to give **22b**, **22c** and **22d**, **22e**, **22f**, respectively. In the case of **22c**, precipitation was observed during the reaction due to the low solubility of the target product in pyrrole and solvents applied, resulting in the relatively low yield of 77%.

Bis(dipyrromethanes) with a biphenylene-linker **23a–d** were successfully synthesized by the same method. The results are listed in Table 5.

Table 4. Synthesis of phenylene-linked bis(dipyrromethanes).



Dialdehyde	Bis(dipyrromethanes)	R^1	R^2	Time [min]	Yield [%]
1	**22a**	H	H	120	93
2	**22b**	Br	H	120	81
3	**22c**	Br	Br	120	77
4	**22d**	OC_4H_9	OC_4H_9	120	90
5	**22e**	OC_7H_{15}	OC_7H_{15}	120	88
6	**22f**	$OC_{10}H_{21}$	$OC_{10}H_{21}$	120	85

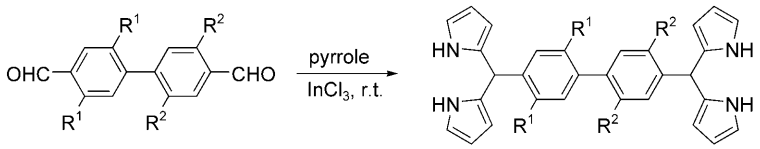
Extension of the method to terphenylene-linked bis(dipyrromethanes) as listed in Table 6 shows that the dialdehydes **16**, **17** and **18** were also compatible with the reaction conditions, and the corresponding products **24a–c** were obtained in good yields.

Notably, the established protocol is also applicable to the synthesis of triphenylenevinylene-linked bis(dipyrromethanes) **25a–c** through the condensation reaction between triphenylenevinylene-linked dialdehydes (**19**–**21**) and pyrrole (Table 7). During the study into the synthesis of triphenylenevinylene-linked bis(dipyrromethanes), we found that such dialdehydes were relatively insoluble in neat pyrrole at room temperature. However, raising the reaction temperature from room temperature to 50 °C could significantly increase the solubility of the starting materials, which facilitated the condensation reaction.

With these novel bis(dipyrromethanes) in hand, we attempted to synthesize novel multiporphyrin arrays by the "2+2" method. Diporphyrin **27** was successfully produced in 12.3% yield through condensation of bis(dipyrromethanes) **22d** with a dipyrromethane-dicarbinol compound derived from **26** *via* a modified procedure (Scheme 3).[6] This yield of **27** was a bit higher than a previous result.[6]

In conclusion, a series of variously functionalized phenylene-linked, biphenylene-linked, triphenylene-linked, and triphenylenevinylene-linked dialdehyde derivatives were synthesized, and the corresponding libraries of novel bis(dipyrromethanes) were prepared by $InCl_3$-catalyzed condensation of those dialdehydes and pyrrole. This protocol has several advantages over published procedures for the synthesis of a large variety of bis(dipyrromethanes), such as high efficiency and great tunability of the linkers, especially useful for the synthesis of multiporphyrin arrays. This work will provide a useful means for the construction of novel multiporphyrin arrays with targeted functionali-

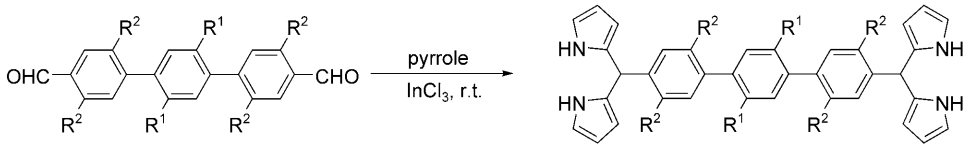
Table 5. Synthesis of biphenylene-linked bis(dipyrromethanes).



Dialdehyde	Bis(dipyrromethanes)	R^1	R^2	Time [min]	Yield [%]
7[a]	**23a**	H	H	120	88
10	**23b**	CH_3	H	120	83
12	**23c**	CH_3	CH_3	120	86
15	**23d**	OC_4H_9	H	120	79

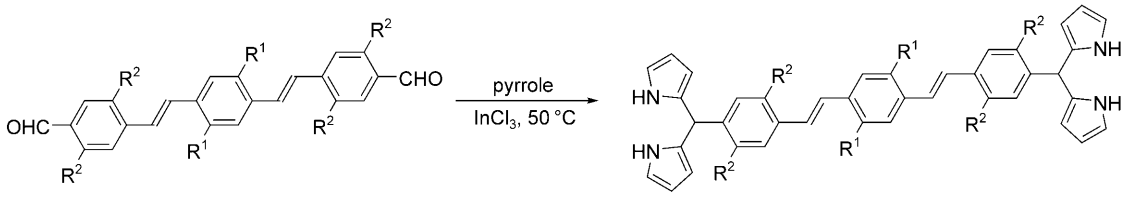
[a] Compound **7** was produced according to a literature procedure.[16]

Table 6. Synthesis of terphenylene-linked bis(dipyrromethanes).



Dialdehyde	Bis(dipyrromethanes)	R^1	R^2	Time [min]	Yield [%]
16	**24a**	CH_3	H	120	73
17	**24b**	CH_3	CH_3	120	78
18	**24c**	$OC_{10}H_{21}$	H	120	75

Table 7. Synthesis of triphenylenevinylene-linked bis(dipyrromethanes).



Dialdehyde	Bis(dipyrromethanes)	R^1	R^2	Time [min]	Yield [%]
19	**25a**	$OC_{10}H_{21}$	H	90	85
20	**25b**	$OC_{10}H_{21}$	OC_4H_9	90	82
21	**25c**	$OC_{10}H_{21}$	$OC_{10}H_{21}$	90	78

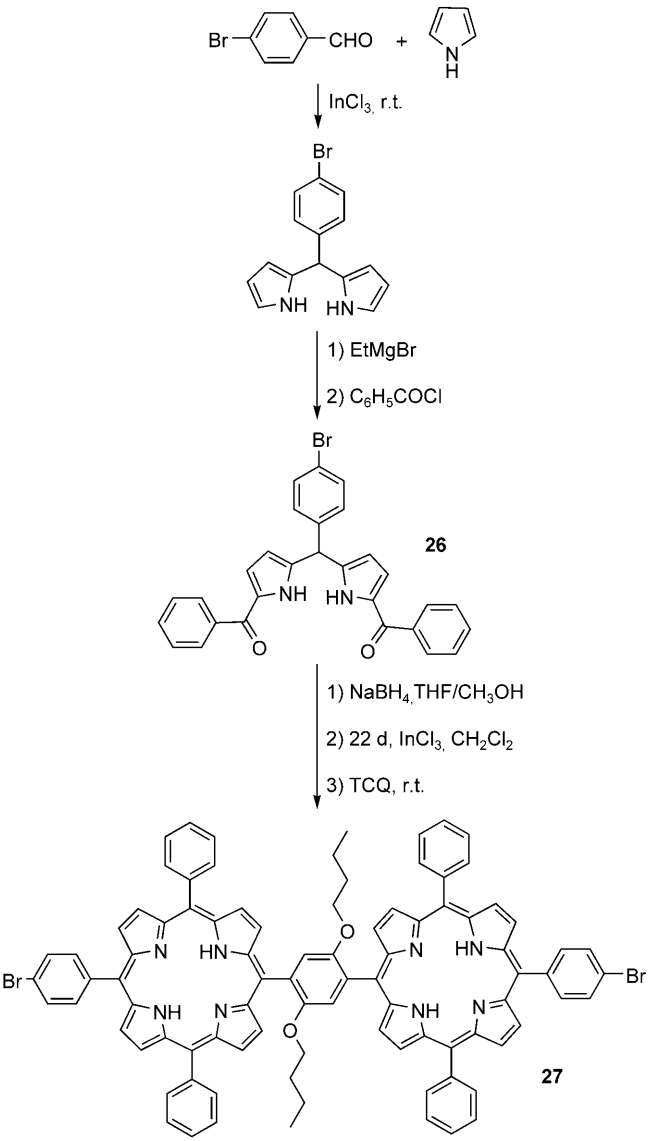
ties, due to the diversity of the well-designed linkers in the critical precursor compounds bis(dipyrromethanes).

Further studies into the synthesis of bis(dipyrromethanes) with other functional groups and the construction of multiporphyrin arrays with numerous porphyrin units from these obtained bis(dipyrromethane) derivatives *via* simultaneous condensation–cyclization–polymerization are in progress in our laboratory.

Experimental Section

General Remarks

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance spectrometer (400 and 100 MHz, respectively). Melting points are uncorrected. The purities of all key intermediates and final products were examined by HLPC analysis. HLPC analysis was carried out with a P680 A instrument using a C18 column (5 μm, 150 mm × 4.6 mm) with detection wavelengths of 220 nm. The solvent was acetonitrile/water (flow rate = 1 mL min^{-1}). The gradient program proceeded



Scheme 3. Synthesis of diporphyrin *via* bis(dipyrromethanes).

from 60% acetonitrile to 90% acetonitrile over 25 min with hold at 90% acetonitrile over 6 min. Mass spectra were obtained *via* matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) without a matrix. Silica gel (40 μm average particle size) was used for column chromatography. Thin layer chromatography was performed by using SiliCycle Silica Gel 60 F_{254} TLC plates and visualized with ultraviolet light. Compounds purchased from Alfa-Aesar were used without further purification. Pyrrole was distilled from CaH_2. THF and toluene were freshly distilled from CaH_2.

Representative Procedure for the Synthesis of Phenylene-Linked Dialdehydes: 2,5-Bis(butoxy)-benzene-1,4-dialdehyde (4) (CAS: 564456-59-3)

It was produced by the same method as for the synthesis of compound **6**,[9] using 1-bromobutane instead of 1-bromodecane during the alkylation. Product **4** was obtained as a yellow solid in 92% yield; mp 87–89 °C (lit. 84–86 °C).[17] ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 10.52$ (s, 2H), 7.43 (s, 2H), 4.08–4.11 (t, 4H), 1.80–1.86 (m, 4H), 1.48–1.54 (m, 4H), 0.97–1.01 (t, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 189.10$, 155.17, 129.34, 111.66, 68.95, 31.04, 19.15, 13.64. MALDI-TOF-MS $m/z = 278.43$ (obs.), calcd. avg. mass: 278.34.

Representative Procedure for the Synthesis of Phenylene-Linked Bis(dipyrromethanes): 2,5-Bis(butoxy)-1,4-bis(dipyrromethan-5-yl)benzene (22d)

By modifying a literature procedure,[7e] the reaction was conducted with dialdehyde **4** (0.28 g, 1.0 mmol) and pyrrole (10.4 mL, 0.15 mol) at room temperature under argon. After stirring for 2 h, powdered NaOH (0.2 g, 5 mmol) was added and the reaction mixture was further stirred for 30 min. The mixture was 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, affording a precipitate. The crude residue was dissolved in a small amount of CH_2Cl_2, and purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2/ethyl acetate = 4:2:1) to give **22d** as a pale brown solid; yield: 0.46 g (90%); 98.15% purity by HLPC; mp 148–150 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.25$ (br, 4H), 6.74 (s, 2H), 6.66 (m, 4H), 6.13 (m, 4H), 5.93 (m, 4H), 5.66 (s, 2H), 3.73–3.76 (t, 4H), 1.54 (m, 4H), 1.27–1.32 (m, 4H), 0.86–0.89 (t, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 150.5, 132.5, 130.7, 116.6, 115.2, 108.2, 106.6, 69.4, 39.1, 31.5, 19.2, 13.8; LC-MS (%): $m/z = 510.6$ (100), calcd.: 510.30; HR-MS: $m/z = 510.2990$, calcd. for $C_{32}H_{38}N_4O_2$ $[M]^+$: 510.2995.

Representative Procedures for the Synthesis of Diporphyrin *via* Bis(dipyrromethanes): 5-(4-Bromophenyl)dipyrromethane (CAS: 159152-11-1)

By modifying a literature procedure,[7e] a mixture of 4-bromobenzaldehyde (1.85 g, 10 mmol) and pyrrole (52 mL, 0.75 mol) was treated with $InCl_3$ (0.2 g, 1.0 mmol) at room temperature under argon. After stirring for 4 h, powdered NaOH (4.0 g, 100 mmol) was added and the reaction mixture was stirred for 45 min. The mixture was filtered. Excess pyrrole was removed by distillation under reduced pressure and the resulting yellow solid was treated with hexanes. The solvent was removed under reduced pressure, affording a precipitate. Recrystallization (CH_3CH_2OH/H_2O) gave a light yellow solid; yield: 2.7 g (89%); mp 123–125 °C (lit. 125.0–125.5 °C).[7e] ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.91$ (br, 2H), 7.42–7.44 (d, 2H), 7.07–7.09 (d, 2H), 6.70 (s, 2H), 6.15–6.16 (d, 2H), 5.88 (s, 2H), 5.43 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 141.30$, 131.95, 131.71, 130.16, 120.85, 117.55, 108.62, 107.52, 43.49. MALDI-TOF-MS: $m/z =$ 301.27 (obs.), calcd. avg. mass: 301.18.

5-(4-Bromophenyl)-1,9-bis(benzoyl)dipyrromethane (26)

By modifying a literature procedure,[6] a solution of 5-(4-bromophenyl)dipyrromethane (3.01 g, 10 mmol) in dry toluene (200 mL) was treated with a solution of EtMgBr (50 mL, 50 mmol, 1.0 M in THF) under argon at room temperature. After stirring for 60 min, a sample of C_6H_5COCl

(2.9 mL, 25 mmol) was added. After stirring for 3 h, the reaction was quenched by adding saturated aqueous NH_4Cl (80 mL). The organic phase was separated, washed with brine and dried over anhydrous Na_2SO_4. After removing the toluene, the resulting crude product was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2/ethyl acetate = 4:2:1), affording a brown solid; 1.25 g (25%); mp 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; MALDI-TOF-MS: *m/z* = 509.00 (obs.), calcd. avg. mass: 509.39.

2,5-Dibutoxy-1,4-bis[10-(4-bromophenyl)-5,15-diphenylporphin-20-yl]benzene (27)

By modifying a literature procedure,[6] a solution of compound **26** (0.509 g, 1.0 mmol) in dry THF/methanol (33 mL, 10:1) was treated with $NaBH_4$ (1.513 g, 40 mmol) at room temperature for 4 h. The reaction mixture was poured into a mixture of saturated aqueous NH_4Cl (80 mL) and CH_2Cl_2 (80 mL). The organic phase was separated, dried over anhydrous Na_2SO_4 and concentrated to dryness. The resulting dipyrromethane-dicarbinol was dissolved in CH_2Cl_2 (200 mL) and 2,5-bis(butoxy)-1,4-bis(dipyrromethan-5-yl)benzene **(22d)** (256 mg, 0.5 mmol) was added under argon at room temperature. After a homogenous solution was obtained, $InCl_3$ (0.238 g, 0.81 mmol) was added and the reaction mixture was stirred at room temperature for 24 h. Chloranil (1.266 g, 5.14 mmol) was added and stirring was continued for 7 h. The mixture was passed through column chromatography (alumina, CH_2Cl_2) and eluted with CH_2Cl_2 until the eluant was no longer dark. The collected eluant was concentrated. The resulting crude product was purified by column chromatography on silica gel (CH_2Cl_2/hexanes = 3:1). Recrystallization ($CHCl_3$/CH_3OH) gave a purplish black solid; yield: 90 mg (12.3%); mp >280 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.33 (m, 4H), 9.03 (m, 4H), 8.91 (m, 4H), 8.86 (m, 4H), 8.30 (m, 8H), 8.14–8.09 (m, 4H), 8.05 (s, 2H), 7.93–7.91 (m, 8H), 7.83 (m, 8H), 3.91–3.88 (t, 4H), 0.98–0.96 (m, 4H), 0.50–0.48 (m, 4H), 0.20–0.16 (t, 6H), −2.62 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.16, 157.59, 151.06, 141.24, 140.38, 139.60, 134.89, 134.87, 133.65, 133.55, 131.51, 130.55, 130.24, 128.92, 128.10, 127.46, 126.81, 125.77, 121.47, 119.90, 119.26, 117.96, 117.55, 115.56, 68.46, 28.69, 17.44, 12.13; MALDI-TOF-MS: *m/z* = 1453.36 (obs.), calcd. avg. mass: 1453.36.

Supporting Information

Experimental procedures and ^{1}H-, ^{13}C NMR and mass spectra for all the other unknown compounds or some important known intermediates obtained *via* modified procedures are available as Supporting Information.

Acknowledgements

We are grateful for financial support to this work from the Natural Science Foundation of Guangdong Province, China (No: 7007735) and the Natural Science Foundation of Hunan Province, China (No: 04JJ40013).

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