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AN IMPROVED SYNTHESIS OF DI-NITRO-FUNCTIONALIZED *TRANS*-A_2B_2-TETRAPHENYLPORPHYRINS

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Abstract – An improved MacDonald-type 2+2 condensation was used to synthesize a series of di-nitro-functionalized *trans*-A_2B_2-tetraphenylporphyrins, and all the structures were characterized by melting point analysis, electronic absorption spectroscopy, infrared spectroscopy, ^{1}H NMR spectroscopy, high-resolution mass spectroscopy, and elemental analysis. The synthesis process was systematically investigated, and several important factors were examined to increase the product yield. The optimum reaction conditions were then established, and the method was found to have the advantages of high reactant concentration, no quinone as oxidant, and good yields of 5,15-bis(*p*-nitrophenyl)-10,20-bis(*p*-R-phenyl)-porphyrins (R = H, F, Cl, Br, Me, and MeO). Moreover, side reactions, such as scrambling, could be suppressed easily by regulating reaction condition.

Among variously substituted *meso*-tetraphenylporphyrins, nitryl-substituted porphyins have always attracted the attention of researchers. The nitro group, which is an important functional group, can be further transformed into various derivatives for different applications. Moreover, *trans*-A_2B_2-porphyins, given their special symmetry structure in the porphyrin macro ring, modified by the nitro group can be used as important precursors making them applicable in artificial photosynthesis,[1-3] chiral catalysts,[4-7]

potential medicines for diagnosis and therapy of cancer,[8-10] dye-sensitized solar cell,[11,12] and polymeric materials.[13]

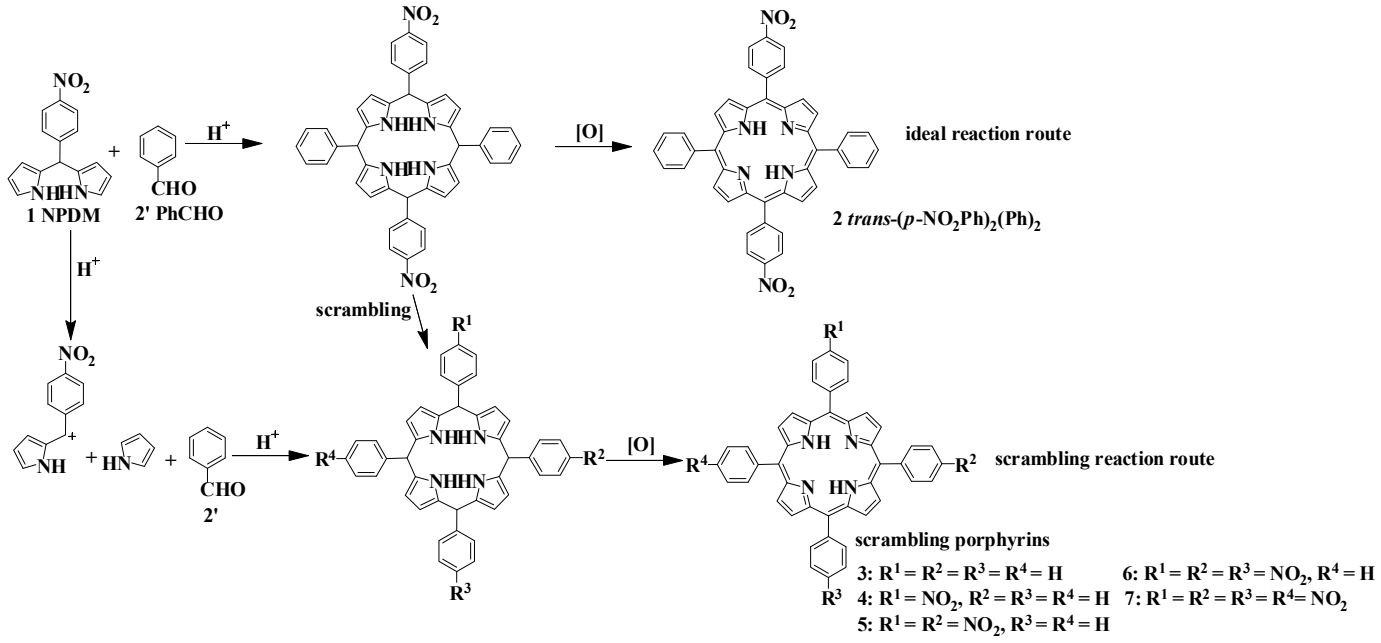
Three kinds of methods are currently used in the synthesis processes to di-nitro-functionalized *trans*-A_2B_2-tetraphenylporphyrin (*trans*-A_2B_2-TPP), including mixed-aldehyde condensation,[14] nitration of *p*-phenyl groups of TPP,[10, 15-17] and MacDonald-type 2+2 condensation.[12,13,18,19] For mixed-aldehyde condensation, the theoretical yield of *trans*-A_2B_2-porphyrin can presently reach a maximum value of 12.5% of total porphyrins. However, 25% A_3B-TPP, 25% AB_3-TPP, 25% *cis*-A_2B_2-TPP, 6.25% A_4-TPP, and 6.25% B_4-TPP in the porphyrins have been achieved as well. Apparently, mixed-aldehyde condensation does not yield *trans*-A_2B_2-TPP as the main product. Furthermore, a significant yield of *cis*-A_2B_2-TPP, composed with the same number of substituents as *trans*-A_2B_2-TPP, have been obtained through the mixed-aldehyde condensation, which would make the separation of *trans*-A_2B_2-TPP from *cis*-A_2B_2-TPP become a difficult task. Kruper *et al*.[15] investigated the nitration of *p*-phenyl groups of TPP to obtain nitro-TPP by using fuming nitric acid. Since then, many researchers[10,16,17,20] improved the nitration condition to obtain mono-, di-, tri-, and tetra-nitro-TPPs selectively. When the nitration was controlled to obtain di-nitro-TPP, the reaction produces *cis*-A_2B_2-TPP as the main product and *trans*-A_2B_2-TPP as the minor product. Zhang *et al*.[21] showed that the electron-withdrawing nitro group would lead to the preferential occurrence of the second nitration to the neighboring phenyl ring, resulting in *cis*-A_2B_2-TPP as the main product. Therefore, the synthesis and separation of di-nitro-functionalized *trans*-A_2B_2-TPP are inconvenient to perform through the methods of mixed-aldehyde condensation or nitration of TPP. In view of the symmetrical structure of *trans*-A_2B_2-TPP, MacDonald-type 2+2 condensation may be a good choice for the synthesis of *trans*-A_2B_2-TPP. Most MacDonald-type 2+2 condensations follow the method of Lindsey *et al*.,[13,18,19] which has relatively low reactant concentrations (only 10 mmol/L) require expensive DDQ or TCQ to oxidize porphyrinogen to porphyrin and is unfavorable for large-scale preparation and resource conversation.[22] Nian Lin *et al*.[23] have recently reported that 5-(*p*-nitrophenyl)dipyrromethane (NPDM (**1**)) directly reacted with benzaldehyde (PhCHO (**2'**)) in refluxing propanoic acid and produced 5,15-bis(*p*-nitrophenyl)-10,20-diphenylporphyrin (*trans*-(*p*-$NO_2Ph)_2(Ph)_2$ (**2**)) with 20% yield. Besides, in the synthesis of symmetric porphyrins, a slight change of condition of solvent, such as mixed solvent of nitroaromatic compound and carboxylic acid, could considerably influence the result of reaction,[22,24] which inspired us to find a more efficient and simple method for the synthesis of di-nitro-functionalized *trans*-A_2B_2-TPP.

In this paper, we present an improved MacDonald-type 2+2 condensation to synthesize di-nitro-functionalized *trans*-A_2B_2-TPP with a high spectral yield up to 31.2%, which was performed with NPDM and aromatic aldehyde dissolved in a mixed solvent of nitrobenzene and acetic acid. The synthesis process was systematically investigated, and several important factors were explored. The optimum

reaction conditions were then established, and the method was found to have the advantages of high reactant concentration, no quinone as oxidant, and good yields of 5,15-bis(*p*-nitrophenyl)-10,20-bis(*p*-R-phenyl)porphyrins (R = H, F, Cl, Br, Me, and MeO). Furthermore, side reactions, such as scrambling, could be suppressed easily by regulating reaction condition.

In this paper, the condensation of NPDM + PhCHO to obtain *trans*-(*p*-$NO_2Ph)_2(Ph)_2$ as the model reaction was investigated. The ideal route of the model reaction is that the acid-catalyzed condensation of NPDM and PhCHO form the corresponding porphyrinogen; and then the porphyrinogen is oxidized to give *trans*-(*p*-$NO_2Ph)_2(Ph)_2$ (Scheme 1). Unfortunately, the decomposition of NPDM and the rearrangement of porphyrinogen would occur under acidic conditions, resulting in scrambling products.[25] Thus, the suppression of the acid-catalyzed scrambling process is the key solution for obtaining more *trans*-(*p*-$NO_2Ph)_2(Ph)_2$.

As can be seen in Scheme 1, the condensation of NPDM + PhCHO and the decomposition of NPDM competed with each other under certain acid-catalyzed condition. The choice of suitable reaction conditions is important, that is, the conditions should be favorable for condensation of NPDM + PhCHO, obtaining *trans*-(*p*-$NO_2Ph)_2(Ph)_2$, and suppressing scrambling porphyrins. Several factors were discussed to determine the optimum conditions for the synthesis of *trans*-(*p*-$NO_2Ph)_2(Ph)_2$.



Scheme 1. The ideal reaction route and scrambling reaction route of NPDM + PhCHO

The effect of reaction temperature was examined in the range from 70 to 145 °C (refluxing temperature). NPDM (1 mmol) and PhCHO (1 mmol) were dissolved in nitrobenzene (10 mL) and reacted under the catalysis of acetic acid (5 mL) for 1 h at a certain temperature. The results, as summarized in Table 1,

show the influence of reaction temperature. The yield of *trans*-(*p*-$NO_2Ph)_2(Ph)_2$ increased with the raising of reaction temperature up to 100 °C. The spectral yield of *trans*-(*p*-$NO_2Ph)_2(Ph)_2$ slightly fluctuated at approximately 30% with the further increase in reaction temperature. High reaction temperature increases the degree of the decomposition of NPDM, producing more scrambling porphyrins and high amounts of tar, which make purification difficult. Thus, the temperature of 100 °C is a good choice because it could suppress decomposition of NPDM and provide a good yield with a relatively low temperature.

Table 1. Influence of reaction temperature[a]

Entry	Reaction temperature (°C)	Spectral yield of *trans*-(*p*-$NO_2Ph)_2(Ph)_2$ (%)
1	70	11.4
2	80	13.2
3	90	23.4
4	100	30.2
5	110	29.6
6	120	30.5
7	130	29.7
8	140	30.2
9	145 (refluxing temperature)	27.7

[a]General condition: 1 mmol NPDM and 1 mmol PhCHO reacted in a mixture of 10 mL nitrobenzene and 5 mL acetic acid under a certain reaction temperature for 1 h.

Table 2. Influence of nitrobenzene and acetic acid[b]

Entry	Nitrobenzene (mL)	Acetic acid (mL)	Spectral yield of *trans*-(*p*-$NO_2Ph)_2(Ph)_2$ (%)
1	0	15	19.9
2	2.5	12.5	22.8
3	5	10	25.6
4	7.5	7.5	26.9
5	10	5	30.2
6	12.5	2.5	13.2
7	15	0	0

[b]General condition: 1 mmol NPDM and 1 mmol PhCHO reacted in a mixture of nitrobenzene and acetic acid ($V_{nitrobenzene} + V_{acetic\ acid} = 15$ mL) under 100 °C for 1 h.

Nitrobenzene amount and acetic acid amount were found to be critical parameters under our reaction conditions. As can be seen in Table 2 (entries 1–5), the addition of suitable amount of nitrobenzene significantly raised the yield of *trans*-(*p*-$NO_2Ph)_2(Ph)_2$ and restrained the generation of tar. However, further increase in nitrobenzene amount would drastically low the yield (entries 5–7). On the other side, without acetic acid, the model reaction would not generate any porphyrin, proving that the condensation of NPDM + PhCHO was an acid-catalyzed process (entry 7). These observations indicate that suitably

relative amounts of nitrobenzene as solvent and acetic acid as catalyst were necessary to accommodate concentration of the acid, which could promote the condensation of NPDM + PhCHO and suppress the decomposition of NPDM. As shown in Table 2, a good yield of *trans*-(*p*-$NO_2Ph)_2(Ph)_2$ can be obtained using 10 mL of nitrobenzene and 5 mL of acetic acid.

The reactant concentration also is an important factor for the condensation of NPDM + PhCHO. Thus, the effects of reactant concentration on the reaction were explored to determine the suitable point with optimum ratio of 2 mL/1 mL of nitrobenzene/acetic acid according to Table 2, and the results are shown in Table 3. The increase in the yield of *trans*-(*p*-$NO_2Ph)_2(Ph)_2$ occurred until the reactant concentration reached 131 mM. However, the yield decreased with the continuous increase in reactant concentration. The results indicate that low concentration was not conducive to the condensation of NPDM + PhCHO, while an excessively high concentration may cause excessive condensation of NPDM + PhCHO, both of which would be adverse to the formation of porphyrinogen. The model reaction produced a high yield at the reactant concentration of 131 mM, which was achieved with 1 mmol of NPDM and 1 mmol of PhCHO in 5 mL of nitrobenzene and 2.5 mL of acetic acid.

Table 3. Influence of reactant concentration[a]

Entry	Reactant concentration (mM)	Spectral yield of *trans*-(*p*-$NO_2Ph)_2(Ph)_2$ (%)
1	6	0.2
2	8	0.6
3	13	5.1
4	33	8.4
5	66	30.2
6	131	31.2
7	263	25.8
8	661	17.4

[a]General condition: 1 mmol NPDM and 1 mmol PhCHO reacted in a certain volume of mixture of nitrobenzene/acetic acid (2/1, V/V) under 100 °C for 1 h.

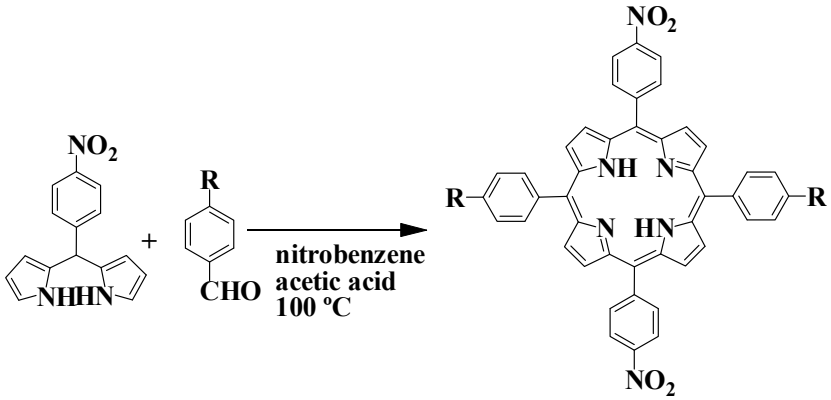
The condensation of NPDM + PhCHO and decomposition of NPDM are acid-catalyzed reactions, and thus, the nature of acid catalyst can significantly affect the selection of the reaction route. A series of straight chain alkyl acids was chosen to investigate the effect of acid catalyst on the model reaction. The condensation of 1 mmol of NPDM and 1 mmol of PhCHO in 5 mL of nitrobenzene was catalyzed by the equimolar of different straight chain alkyl carboxylic acids. The results are provided in Table 4. Formic acid, which can promote the decomposition of NPDM, produced large numbers of scrambling porphyrins and only 1.6% of *trans*-(*p*-$NO_2Ph)_2(Ph)_2$. From acetic acid to *n*-heptanoic acid, the yield of *trans*-(*p*-$NO_2Ph)_2(Ph)_2$ decreased with the increase in the lengths of alkyl chain of acid catalysts.

Interestingly, *n*-hexanoic acid or *n*-heptanoic acid, weak acid catalyst, which would suppress the condensation of NPDM + PhCHO to leading a bad yield of *trans*-(*p*-$NO_2Ph)_2(Ph)_2$, suppress the decomposition of NPDM to resulting in less scrambling porhyrins and was conducive to the separation of *trans*-(*p*-$NO_2Ph)_2(Ph)_2$. In view of the scrambling effect and the yield of *trans*-(*p*-$NO_2Ph)_2(Ph)_2$, acetic acid was selected as the acid catalyst in the following study.

Table 4. The influence of different acid catalyst[a]

Entry	Acid catalyst	Spectral yield of *trans*-(*p*-$NO_2Ph)_2(Ph)_2$ (%)
1	formic acid	1.6
2	acetic acid	31.2
3	propionic acid	27.6
4	*n*-butyric acid	26.6
5	*n*-valeric acid	18.0
6	*n*-hexanoic acid	17.2
7	*n*-heptanoic acid	15.3

[a]General condition: 1 mmol NPDM and 1 mmol PhCHO reacted in a mixture of 5 mL nitrobenzene and a certain volume straight chain alkyl carboxylic acid (with equimolar of 2.5 mL acetic acid) under 100 °C for 1 h.



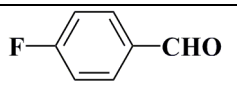
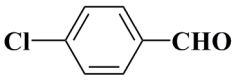
1

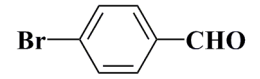
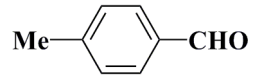
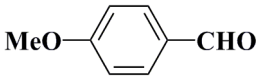
8': R = F
9': R = Cl
10': R = Br
11': R = Me
12': R = MeO

8: R = F
9: R = Cl
10: R = Br
11: R = Me
12: R = MeO

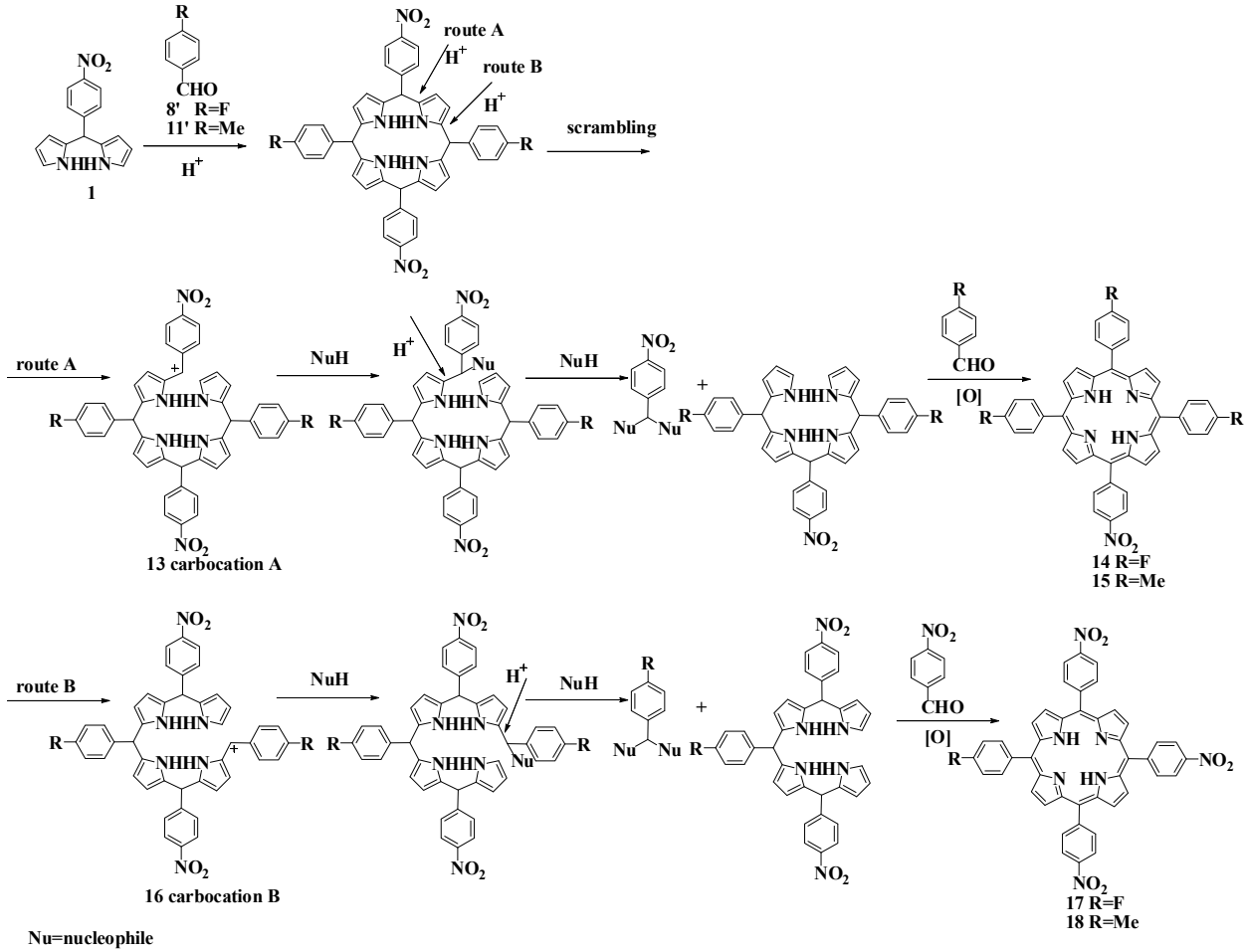
Scheme 2. Synthesis of various 5,15-bis(*p*-nitrophenyl)-10,20-bis(*p*-R-phenyl)porphyrins

Table 5. Reaction of NDPM with different aromatic aldehydes in the optimized proceduce

	Aldehyde	Product	Isolated Yield (%)
1		5,15-bis(*p*-nitrophenyl)-10,20-bis(*p*-fluorophenyl)-porphyrin	25.1
2		5,15-bis(*p*-nitrophenyl)-10,20-bis(*p*-chlorophenyl)-porphyrin	20.3

3		5,15-bis(*p*-nitrophenyl)-10,20-bis(*p*-bromophenyl)-porphyrin	19.7
4		5,15-bis(*p*-nitrophenyl)-10,20-bis(*p*-methylphenyl)-porphyrin	24.3
5		5,15-bis(*p*-nitrophenyl)-10,20-bis(*p*-methoxyphenyl)-porphyrin	24.2

As discussed above, the preferred reaction condition includes 1 mmol of NPDM and 1 mmol of PhCHO in 5 mL of nitrobenzene and 2.5 mL of acetic acid at 100 °C for 1 h, which could give a spectral yield of 31.2% of *trans*-(p-$NO_2Ph)_2(Ph)_2$ (with isolated yield of 26.0%). Only a small amount of scrambling porphyrins was found. The reasons for the efficient suppressing scrambling are as follows: 1. the nitro group of NDPM, as electron-withdrawing group, made the decomposition of NDPM difficult,[19] and 2. the suitable reaction condition resulted in the desired reaction route. Furthermore, the degree of scrambling should be high relative to the nature of the used aldehyde. Then, the optimized procedure was repeated for the preparation of 5,15-bis(*p*-nitrophenyl)-10,20-bis(*p*-R-phenyl)porphyrins (**8-12**) from NDPM and aromatic aldehydes (**8'-12'**) (Scheme 2 and Table 5).



Scheme 3. Two probable scrambling routes of porphyrinogen

The isolated yields of 5,15-bis(*p*-nitrophenyl)-10,20-bis(*p*-R-phenyl)porphyrins fluctuated between 20% and 25%, indicating that the substituent had insignificant electronic effect on the yield of 5,15-bis(*p*-nitrophenyl)-10,20-bis(*p*-R-phenyl)porphyrin. However, the electronic effect of the substituent affected the degree of scrambling. Small amounts of 5,10,15-tri(*p*-nitrophenyl)-20-(*p*-fluorophenyl)porphyrin (**17**) and 5-(*p*-nitrophenyl)-10,15,20-tri-(*p*-fluorophenyl)porphyrin (**14**) were observed in the NPDM + *p*-fluorobenzaldehyde (**8'**); while no 5-(*p*-nitrophenyl)-10,15,20-tri(*p*-methylphenyl)porphyrin (**15**) generated from NPDM + *p*-methylbenzaldehyde (**11'**), but a small amount of 5,10,15-tri(*p*-nitrophenyl)-20-(*p*-methylphenyl)porphyrin (**18**) was found. Different degrees of scrambling observed in the NPDM + aromatic aldehydes might imply different reaction route for each.

The different degrees of scrambling of NPDM + aromatic aldehydes might follow the mechanism shown in Scheme 3.[26] For the aromatic aldehyde with electron-releasing group, such as Me, the scrambling tended to route B, generating more stable carbocation B (**16**) intermediate and resulting in the formation of 5,10,15-tri(*p*-nitrophenyl)-20-(*p*-methylphenyl)porphyrin (**18**). For the aromatic aldehyde with electron-withdrawing group, such as F, although scrambling mainly followed route B, with improving the stability of carbocation A (**13**) intermediate, the probability of scrambling via route A increased, and resulting in the formation of 5-(*p*-nitrophenyl)-10,15,20-tri(*p*-fluorophenyl)porphyrin (**14**).

In summary, we developed a simple method of using the mixed solvent of nitrobenzene and acetic acid to synthesize 5,15-bis(*p*-nitrophenyl)-10,20-bis(*p*-R-phenyl)porphyrin. The method allowed high reactant concentration (131 mmol/L) and generated a good yield of 5,15-bis(*p*-nitrophenyl)-10,20-bis(*p*-R-phenyl)porphyrin, but it did not require quinone as oxidant. Furthermore, we found that the degree of scrambling could be controlled by selecting the suitable reaction condition and that the electronic effect of the substituents would affect the route of scrambling, which could cause the formation of different scrambling porphyrins.

EXPERIMENTAL

Melting points were recorded on SGW X-4B melting-point apparatus and are uncorrected. The ^{1}H NMR spectra were obtained using a Bruker AV 400 M spectrometer in solvent ($CDCl_3$/TFA) with TMS as internal reference. Electronic absorption spectra were measured using a UV1901 spectrophotometer (Shanghai Phenix). High resolution mass spectra (ESI) were obtained on a Bruker micrOTOF-QII. Infrared spectra (IR) were recorded as thin films on KBr plates with a Bruker Vertex 70 spectrometer. Elemental analysis was performed on a Euro Vector EA3000. Column chromatography was performed using silica gel (300-400 mesh) produced by Qingdao Marine Chemical Factory, Qingdao (China). Commercially available solvents and reagents were used without further purification. The NDPM that was not commercially available was synthesized following procedures described in the literature.[27]

General method for the synthesis of 5,15-bis(*p*-nitrophenyl)-10,20-bis(*p*-R-phenyl)porphyrin

1 mmol NDPM and 1 mmol aromatic aldehyde were added to a mixture of 5 mL nitrobenzene and 2.5 mL acetic acid preheated to 100 °C. After 1 h of stirring, the mixture was cooled to room temperature. Then, nitrobenzene and acetic acid were evaporated under reduced pressure, and the residue was purified by silica gel column chromatography with mixture of CH_2Cl_2 and *n*-hexane. After evaporation, the crude product was washed with methanol via centrifugation, resulting in pure 5,15-bis(*p*-nitrophenyl)-10,20-bis(*p*-R-phenyl)porphyrin.

General method for measuring the spectral yield of 5,15-bis(*p*-nitrophenyl)-10,20-diphenylporphyrin (2)

The solutions, which concentrations ranged from 1.0217 to 2.0434 × 10^{-6} mol/L, were prepared by dissolving and diluting purified 5,15-bis(*p*-nitrophenyl)-10,20-diphenylporphyrin with CH_2Cl_2 as solvent. According to the Beer-Lambert law, the linear regression equation as A = 298508C + 0.0399 (the regression coefficient R^2 = 0.9997) could be constructed by the concentration (C (mol/L)) and the corresponding absorbance (A) of the Soret band (λ_{max} = 420.1 nm) of 5,15-bis(*p*-nitrophenyl)-10,20-diphenylporphyrin solution. Subsequently, the unknown concentration of the diluted crude product of 5,15-bis(*p*-nitrophenyl)-10,20-diphenylporphyrin could be found with the measured absorbance via the linear regression equation, and then the corresponding spectral yield could be acquired by relevant calculation.

5,15-Bis(*p*-nitrophenyl)-10,20-diphenylporphyrin (2)

Purple powder. Spectral yield 31.2% (isolate yield 26.0%). Mp >300 °C. UV-vis (CH_2Cl_2) λ_{max}/nm (logε): 420.1 (5.48), 515.9 (4.41), 551.9 (4.20), 590.4 (4.07), 646.5 (4.03). IR (KBr): 3317.95, 3101.63, 3070.84, 1595.00, 1558.79, 1516.04, 1472.54, 1400.30, 1344.14, 1223.13, 1186.39, 1107.42, 1018.78, 965.16, 847.26, 801.04, 746.92, 725.72, 700.42 cm^{-1}. HRMS (ESI): *m/z* $[M+H]^+$ calculated for $C_{44}H_{28}N_6O_4$+H: 705.2245, found: 705.2183. ^1H NMR (400 MHz, $CDCl_3$/TFA) δ 8.900 (d, *J* = 8.4 Hz, 4 H), 8.793 (d, *J* = 8.4 Hz, 4 H), 8.765 (d, *J* = 4.8 Hz, 4 H), 8.688 (d, *J* = 4.8 Hz, 4 H), 8.574 (t, *J* = 3.6 Hz, 4 H), 8.068 (d, *J* = 4.8 Hz, 6 H), -0.417 (s, 4 H). Anal. Calcd for $C_{44}H_{28}N_6O_4$: C 74.99, H 4.00, N 11.93. Found: C 72.71, H 4.07, N 11.40.

5,15-Bis(*p*-nitrophenyl)-10,20-bis(*p*-fluorophenyl)porphyrin (8)

Purple powder. Isolated yield 25.1%. Mp >300 °C. UV-vis (CH_2Cl_2) λ_{max}/nm (logε): 419.8 (5.53), 515.9 (4.47), 551.8 (4.25), 590.4 (4.12), 645.9 (4.05). IR (KBr): 3318.29, 3107.17, 3075.98, 1596.51, 1559.67, 1519.53, 1473.82, 1400.08, 1347.49, 1224.38, 1157.47, 1108.10, 1016.67, 966.67, 850.52, 798.31, 729.10 cm^{-1}. HRMS (ESI): *m/z* $[M+H]^+$ calculated for $C_{44}H_{26}F_2N_6O_4$+H: 741.2056, found: 741.1959. ^1H NMR (400 MHz, $CDCl_3$/TFA) δ 8.900 (d, *J* = 8.4 Hz, 4 H), 8.775 (d, *J* = 8.4 Hz, 4 H), 8.731 (d, *J* = 4.8 Hz, 4 H), 8.694 (d, *J* = 4.8 Hz, 4 H), 8.564 (dd, J_1 = 8.4 Hz, J_2 = 5.2 Hz, 4 H), 7.781 (t, *J* = 8.4 Hz, 4 H), -0.350

(s, 4 H). Anal. Calcd for $C_{44}H_{26}F_2N_6O_4$: C 71.35, H 3.54, N 11.35. Found: C 70.71, H 3.82, N 10.91.

5,15-Bis(*p*-nitrophenyl)-10,20-bis(*p*-chlorophenyl)porphyrin (9)

Purple powder. Isolated yield 20.3%. Mp >300 °C. UV-vis (CH_2Cl_2) λ_{max}/nm (logε): 420.7 (5.28), 515.9 (4.13), 552.1 (3.85), 589.7 (3.69), 646.5 (3.58). IR (KBr): 3320.08, 3102.71, 3073.31, 1594.79, 1559.88, 1517.25, 1472.24, 1397.42, 1345.46, 1216.57, 1178.40, 1091.68, 1017.14, 965.92, 849.30, 800.98, 734.54 cm^{-1}. HRMS (ESI): *m/z* $[M+H]^+$ calculated for $C_{44}H_{26}Cl_2N_6O_4$+H: 773.1465, found: 773.1350. ^1H NMR (400 MHz, $CDCl_3$/TFA) δ 8.905 (d, *J* = 8.4 Hz, 4 H), 8.773 (d, *J* = 8.4 Hz, 4 H), 8.745 (d, *J* = 4.4 Hz, 4 H), 8.695 (d, *J* = 4.4 Hz, 4 H), 8.509 (d, *J* = 8.0 Hz, 4 H), 8.063 (d, *J* = 8.0 Hz, 4 H), -0.357 (s, 4 H). Anal. Calcd for $C_{44}H_{26}Cl_2N_6O_4$: C 68.31, H 3.39, N 10.86. Found: C 69.77, H 3.70, N 10.12.

5,15-Bis(*p*-nitrophenyl)-10,20-bis(*p*-bromophenyl)porphyrin (10)

Purple powder. Isolated yield 19.7%. Mp >300 °C. UV-vis (CH_2Cl_2) λ_{max}/nm (logε): 421.0 (5.49), 516.0 (4.39), 551.7 (4.17), 590.4 (4.05), 645.9 (3.97). IR (KBr): 3321.31, 3101.22, 3076.35, 1595.25, 1560.17, 1518.67, 1472.36, 1393.16, 1345.83, 1220.34, 1182.67, 1105.61, 1013.07, 966.11, 848.89, 799.35, 732.38 cm^{-1}. HRMS (ESI): *m/z* $[M+H]^+$ calculated for $C_{44}H_{26}Br_2N_6O_4$+H: 863.0440, found: 863.0328. ^1H NMR (400 MHz, $CDCl_3$/TFA) δ 8.900 (d, *J* = 8.8 Hz, 4 H), 8.772 (d, *J* = 8.8 Hz, 4 H), 8.736 (d, *J* = 4.8 Hz, 4 H), 8.684 (d, *J* = 4.8 Hz, 4 H), 8.433 (d, *J* = 8.4 Hz, 4 H), 8.220 (d, *J* = 8.4 Hz, 4 H), -0.166 (s, 4 H). Anal. Calcd for $C_{44}H_{26}Br_2N_6O_4$: C 61.27, H 3.04, N 9.74. Found: C 60.85, H 3.34, N 9.38.

5,15-Bis(*p*-nitrophenyl)-10,20-bis(*p*-methylphenyl)porphyrin (11)

Purple powder. Isolated yield 24.3%. Mp >300 °C. UV-vis (CH_2Cl_2) λ_{max}/nm (logε): 421.2 (5.49), 517.1 (4.43), 553.1 (4.25), 591.7 (4.08), 647.5 (4.05). IR (KBr): 3319.42, 3104.01, 3075.62, 3020.47, 2919.36, 2851.40, 1595.46, 1560.35, 1517.10, 1473.35, 1400.09, 1345.63, 1220.87, 1183.83, 1108.77, 1019.98, 966.12, 848.03, 800.06, 726.93 cm^{-1}. HRMS (ESI): *m/z* $[M+H]^+$ calculated for $C_{46}H_{32}N_6O_4$+H: 733.2558, found: 733.2479. ^1H NMR (400 MHz, $CDCl_3$/TFA) δ 8.896 (d, *J* = 8.8 Hz, 4 H), 8.804 (d, *J* = 8.4 Hz, 4 H), 8.725 (d, *J* = 4.8 Hz, 4 H), 8.646 (d, *J* = 4.8 Hz, 4 H), 8.481 (d, *J* = 8.0 Hz, 4 H), 7.880 (d, *J* = 7.6 Hz, 4 H), 2.825 (s, 6 H), -0.014 (s, 4 H). Anal. Calcd for $C_{46}H_{32}N_6O_4$: C 75.40, H 4.40, N 11.47. Found: C 72.59, H 4.21, N 10.39.

5,15-Bis(*p*-nitrophenyl)-10,20-bis(*p*-methoxyphenyl)porphyrin (12)

Purple powder. Isolated yield 24.2%. Mp >300 °C. UV-vis (CH_2Cl_2) λ_{max}/nm (logε): 423.4 (5.58), 518.2 (4.49), 555.5 (4.38), 592.9 (4.23), 649.0 (4.22). IR (KBr): 3315.23, 3103.62, 3072.92, 2928.43, 2835.77, 1595.44, 1557.91, 1515.69, 1473.13, 1400.70, 1345.94, 1287.45, 1247.60, 1175.78, 1107.32, 1031.93, 965.67, 848.84, 798.66, 727.95 cm^{-1}. HRMS (ESI): *m/z* $[M+H]^+$ calculated for $C_{46}H_{32}N_6O_6$+H: 765.2456, found: 765.2385. ^1H NMR (400 MHz, $CDCl_3$/TFA) δ 8.886 (d, *J* = 8.4 Hz, 4 H), 8.783 (d, *J* = 8.8 Hz, 4 H), 8.690 (d, *J* = 4.8 Hz, 4 H), 8.638 (d, *J* = 4.8 Hz, 4 H), 8.514 (d, *J* = 8.4 Hz, 4 H), 7.595 (d, *J* = 8.8 Hz, 4 H), 4.195 (s, 6 H), -0.268 (*s*, 4 H). Anal. Calcd for $C_{46}H_{32}N_6O_6$: C 72.24, H 4.22, N 10.99. Found: C

72.32, H 4.49, N 10.52.

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REFERENCES

1. T. A. Moore, D. Gust, P. Mathis, J.-C. Mialocq, C. Chachaty, R. V. Bensasson, E. J. Land, D. Doizi, P. A. Liddell, W. R. Lehman, G. A. Nemeth, and A. L. Moore, *Nature*, 1984, **307**, 630.
2. G. Steinberg-Yfrach, J.-L. Rigaud, E. N. Durantini, A. L. Moore, D. Gust, and T. A. Moore, *Nature*, 1998, **392**, 479.
3. M. Hambourger, G. F. Moore, D. M. Kramer, D. Gust, A. L. Moore, and T. A. Moore, *Chem. Soc. Rev.*, 2009, **38**, 25.
4. S. Zhu, J. V. Ruppel, H. Lu, L. Wojtas, and X. P. Zhang, *J. Am. Chem. Soc.*, 2008, **130**, 5042.
5. Y. Chen, J. V. Ruppel, and X. P. Zhang, *J. Am. Chem. Soc.*, 2007, **129**, 12074.
6. Y. Chen and X. P. Zhang, *J. Org. Chem.*, 2007, **72**, 5931.
7. Y. Chen, K. B. Fields, and X. P. Zhang, *J. Am. Chem. Soc.*, 2004, **126**, 14718.
8. D. Kessel, R. Luguya, and M. G. H. Vicente, *Photochem. Photobiol.*, 2003, **78**, 431.
9. G. G. Meng, B. R. James, and K. A. Skov, *Can. J. Chem.-Rev. Can. Chim.*, 1994, **72**, 1894.
10. R. Luguya, L. Jaquinod, F. R. Fronczek, M. G. H. Vicente, and K. M. Smith, *Tetrahedron*, 2004, **60**, 2757.
11. M. G. Walter, C. C. Wamser, J. Ruwitch, Y. Zhao, D. Braden, M. Stevens, A. Denman, R. Pi, A. Rudine, and P. J. Pessiki, *J. Porphyr. Phthalocyanines*, 2007, **11**, 601.
12. M. E. Milanesio, M. Gervaldo, L. A. Otero, L. Sereno, J. J. Silber, and E. N. Durantini, *J. Porphyr. Phthalocyanines*, 2003, **7**, 42.
13. W. Anannarukan, S. Tantayanon, D. Zhang, E. A. Alemán, D. A. Modarelli, and F. W. Harris, *Polymer*, 2006, **47**, 4936.
14. J. S. Lindsey, 'The Porphyrin Handbook', Vol. 1, ed. by K. M. Kadish, K. M. Smith, and R. Guilard, Academic Press, San Diego, CA, 2000, pp. 45-118.
15. W. J. Kruper, T. A. Chamberlin, and M. Kochanny, *J. Org. Chem.*, 1989, **54**, 2753.
16. S. Ostrowski and B. Łopuszyńska, *Synth. Commun.*, 2003, **33**, 4101.

17. N. W. Smith and S. V. Dzyuba, *ARKIVOC*, 2010, **vii**, 10.
18. B. J. Littler, Y. Ciringh, and J. S. Lindsey, *J. Org. Chem.*, 1999, **64**, 2864.
19. C. Frixa, M. F. Mahon, A. S. Thompson, and M. D. Threadgill, *Org. Biomol. Chem.*, 2003, **1**, 306.
20. Z. Xue, P. P. S. Lee, Y. Wang, D. W. J. Kwong, J. Li, J. H. Xin, W.-K. Wong, and K. K. L. Cheuk, *Tetrahedron*, 2011, **67**, 6030.
21. H.-L. Zhang, W.-M. Shi, and J. Wu, *Heterocycles*, 2005, **65**, 3001.
22. R. A. W. Johnstone, M. L. P. G. Nunes, M. M. Pereira, A. M. d'A. Rocha Gonsalves, and A. C. Serra, *Heterocycles*, 1996, **43**, 1423.
23. T. Lin, X. S. Shang, J. Adisoejoso, P. N. Liu, and N. Lin, *J. Am. Chem. Soc.*, 2013, **135**, 3576.
24. A. C. Serra and A. M. d'A. Rocha Gonsalves, *Tetrahedron Lett.*, 2010, **51**, 4192.
25. D. M. Wallace, S. H. Leung, M. O. Senge, and K. M. Smith, *J. Org. Chem.*, 1993, **58**, 7245.
26. H. K. Hombrecher, G. Horter, and C. Arp, *Tetrahedron*, 1992, **48**, 9451.
27. T. Rohand, E. Dolusic, T. H. Ngo, W. Maes, and W. Dehaen, *ARKIVOC*, 2007, **x**, 307.