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A More Efficient Synthetic Route to Perylene-porphyrin Arrays

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Abstract: We present an efficient synthetic route towards two kinds of perylene-porphyrin arrays. Starting from 5, 10, 15, 20-*meso*-tetraphenylporphyrin, two novel **9a** and **9b** were designed and synthesized with 40.3% and 35.1% yield, respectively.

Keywords: Perylene-porphyrin arrays, photoinduced charge transfer, molecular switch.

The development of porphyrin arrays with the potential to undergo controlled energy or electron transfer has led to the production of prototypical molecular-scale devices such as wires, logic devices, switches and gates[1,2,3], essential for the miniaturization of electronic componentry and technology. Wasielewski and coworkers[2] have pioneered the synthesis of perylene-porphyrin array in which the electron acceptor perylene was covalently bonded to two porphyrins with a phenyl linker (**Scheme 1**). However, the yield of the expected array was very low (<0.4%) because the condensation of pyrrole with the mixture of 1-hexanal and *p*-nitrobenzaldehyde would give six products, which were difficult to separate and purify to obtain *meso*-tripentyl-mono-(*p*-nitrophenyl)porphyrin. Considering the great significance of perylene-porphyrin arrays shown by Wasielewski and Lindsy's groups[2, 4], it is necessary to explore an effective route to prepare these arrays. Here we report a new efficient synthetic route (**Scheme 2**) to prepare perylene-porphyrin arrays with the yield, which is over 30 times than that of the literature method[2]. Our strategy is as follows:

According to literature[5], **2a**[7] and **2b** were prepared by condensing **1** with *n*-butylamine and *n*-dodecylamine in yield of 40.3% and 25.5%, respectively. **7** was often obtained by condensing pyrrole with the mixture of benzaldehyde and *p*-nitro-benzaldehyde, which is similar to the method of Wasielewski *et al*[2]. The yield of mono-nitrified product **7** was no more than 1%. We modified this route through direct nitration of 5, 10, 15, 20–tetraphenylporphyrin **6**[6], which was obtained in a yield of 35.2% by convenient condensation of pyrrole and benzaldehyde in chloroacetic acid and xylol under reflux. When **6** consumed completely, the reaction mixture was neutralized with dilute ammonium hydroxide. The dark brown solution was washed with 5×400 mL water and the separated organic layer was collected. After drying over anhydrous

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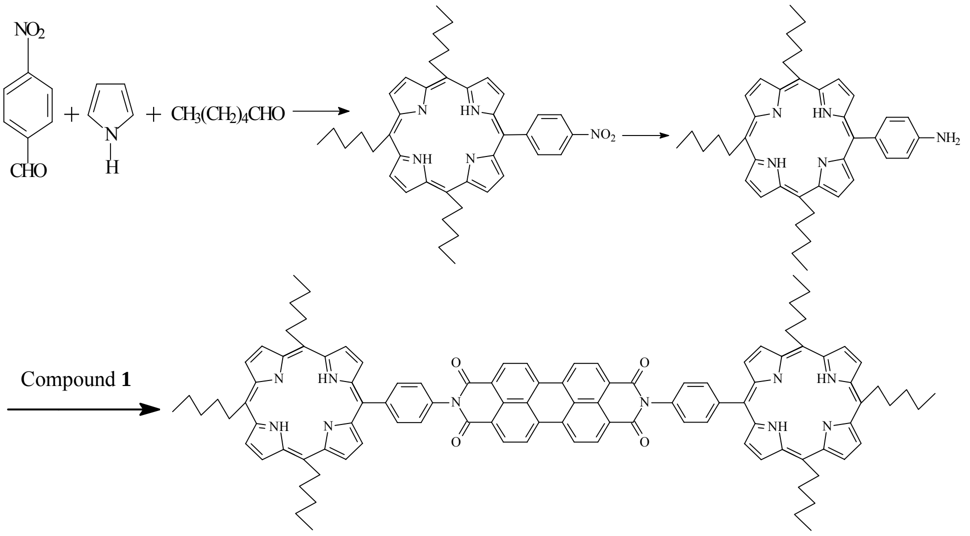
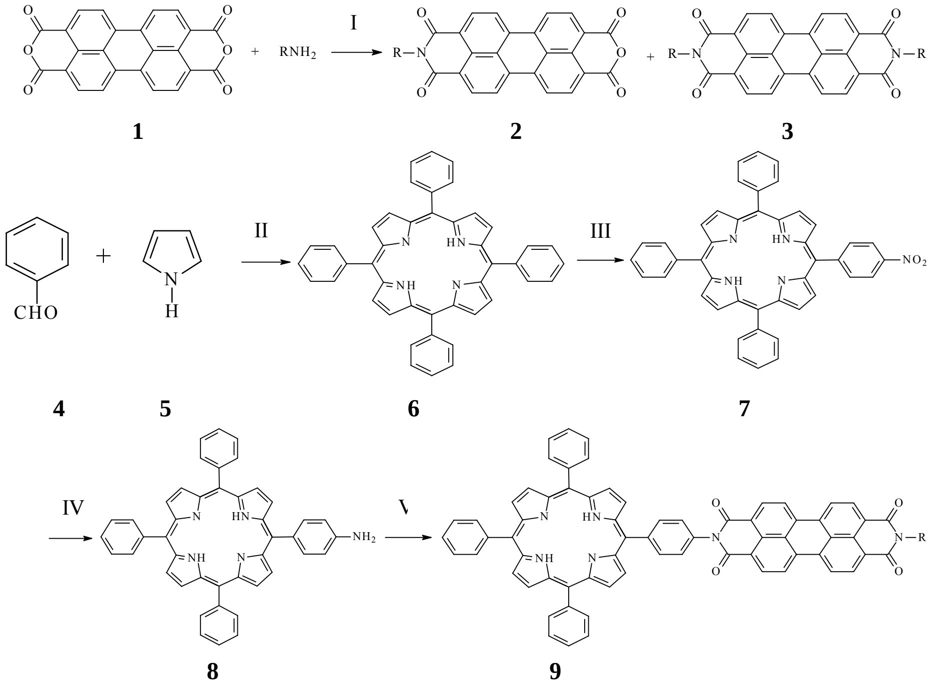
Scheme 1



Scheme 2



R= $CH_2(CH_2)_2CH_3$(a) or $CH_2(CH_2)_{10}CH_3$(b)

Regents and conditions: I) 2a: H_2O, 58-60°C, 3h; 2b: H_2O:n-PrOH=1:1, 3h; II) $ClCH_2COOH$, xylol, reflux; III) fuming nitric acid, $CHCl_3$, 0-5°C; IV) $SnCl_2.2H_2O$, HCl, 65-70°C; V)**2a** or **2b**, Imidazole, *m*-cresol, 170-175°C sodium sulfate the solution was concentrated to 50-70 mL and purified on a silica gel column eluting with chloroform. The first dark brown band containing **7** was collected. The eluate was evaporated to dryness, the solid sample was recrystallized from 5:1 mixture of $CHCl_3$/MeOH and the raw product **7** was obtained in a yield of 58.8%.

Reduction of **7** was performed according to a method described by Kruper *et al.*[6]. 2.0 g of **7** was dissolved in 100 mL of concentrated hydrochloric acid into which 3.0 g of tin (II)-chloride dihydrate was added subsequently. The obtained green solution was heated to 65-70℃ with stirring for 1.5 h. After cooling, 250 mL of water was added into the solution and green solid was separated out by filtration. The solid was dispersed in 150 mL water then dilute ammonium hydroxide was added to bring the pH of suspension to 8-9. The brown-violet mixture was extracted with 3×300 mL portions of chloroform. The organic layer was separated, filtered, washed with water, then dried over anhydrous sodium sulfate and evaporated to dryness. The product was purified on a silica gel column with $CHCl_3$ as eluent. The first band was collected and the yield of **8** was 89.4%.

2a (0.447g), **8** (0.630g) and imidazole (0.50g) were dissolved in 25 mL *m*-cresol in nitrogen atmosphere. The solution was heated to 170-175℃ and stirred for 24 hrs; after cooled to 100℃ it was poured into 150 mL methanol. The precipitate was collected by filtration and washed with methanol several times. The cake was repeatedly dispersed in 1% hot potassium hydroxide, and filtered to remove soluble precipitate of **2a**. Then the crude product was dissolved in 100 mL chloroform and stirred overnight. The derived purple precipitate **9a** was filtered, **8** left in filterate. The solid was dissolved in 30 mL hot *m*-cresol and poured into methanol again. The resulting precipitate was washed repeatedly with hot aqueous potassium hydroxide (1%) solution, followed by water and methanol. After drying under vacuum at 100℃ overnight, the product **9a**[7, 8, 9] was obtained as a dark red-violet solid (76.7% based on **8**). **9b** was synthesized by the same procedures in the yield of 66.7%.

Benzaldehyde was condensed with pyrrole to obtain **6** in 35.2% yields. **6** was nitrified directly to give mono-nitrified tetraphenylporphyrin **7** in 58.8% yields. **7** was reduced with $SnCl_2 \cdot 2H_2O$ to give corresponding monoamine **8** in 89.4%. **8** was reacted with **2** to obtain expected arrays **9a** and **9b** in yield of 14.2% and 12.3%, which were calculated from pyrrole (30.9% and 28.9% from compound **1**), respectively. The products were fully characterized by IR, UV, element analysis and ^1H NMR. From the fluorescence spectrum, **9a** and **9b** exhibit ultrafast photoinduced charge transfer rather than energy transfer. The investigation on the photochemical and photophysical properties of these molecular arrays and the synthesis of other perylene-porphyrin arrays are in progress.

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References and Notes

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7. Selected data of **2a**: red crystals, Calcd. for $C_{28}H_{17}NO_5$: C, 75.16, H, 3.83, N, 3.13; Found C, 74.91, H, 3.75, N, 3.08. IR (KBr, cm^{-1}): 1766.5, 1723.8 (-C=O, anhydrides); 1694.8, 1655.8 (-C=O, imides); λ_{abs} (NMP): 458, 489, 524nm.

   Selected data of **9a**: dark red-violet solid, Calcd. for $C_{72}H_{46}N_6O_4$: C, 81.65, H, 4.38, N, 7.93; Found (also see ref. 7) C, 80.04, H, 4.15, N, 7.79; IR (ν, KBr): 1699.0, 1660.4(-C=O, imides); ^{1}H NMR ($CDCl_3/CF_3COOD$=10:1; δ, ppm)(also see ref. 8) 1.05-1.02 (m, 3H), 1.49-1.54 (m, 2H), 1.79- 1.82 (m, 2H), 4.29-4.32 (m, 2H), 8.06-8.11 (m, 11H), 8.57-8.58 (m,6H), 8.78-8.91 (m, 14H), 8.96-8.97 (m, 2H), 9.04-9.05(m, 2H); λ_{abs} ($CHCl_3$): 418, 459, 490, 527, 591, 645 nm.

   Selected data of **9b**: dark red-violet solid, Calcd. for $C_{80}H_{62}N_6O_4$: C, 82.03, H, 5.33, N, 7.17; Found: C, 81.45, H, 5.32, N, 6.89; FT-IR (KBr, cm^{-1}) 1699.4, 1668.1(-C=O, imides); ^{1}H NMR ($CDCl_3/CF_3COOD$=10:1; δ, ppm) 0.88-0.90(m, 3H), 1.28-1.32(m, 14H), 1.41(m, 2H), 1.48 (m, 2H), 1.81 (m, 2H), 4.30 (m, 2H), 8.08-8.12 (m, 11H), 8.58-8.59 (m, 6H), 8.80-8.89 (m, 14H), 8.94-8.97(m, 2H), 9.06-9.08(m, 2H); λ_{abs}($CHCl_3$): 418, 459, 491, 527, 591, 645nm.
8. The differences between the calculated and found number of element analysis were found possibly due to the adsorbed solvent which is difficulty to remove.
9. Two protons (under high field) on N atom of pyrrole were exchanged by D atom of CF_3COOD.

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