Supplementary Information

Synthesis of Novel Porphyrin Derivatives with Mesogenic Properties

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Table of contents

1. General information	2
2. Experimentation section	2-4
3. MS, ¹ H NMR and IR Spectra of the Products	4-10

1. General information

Pyrrole was newly distilled before use because of its self-polymerization. Methyl 4-formylbenzoate and propionic acid were purchased and used without further purification. The MS was recorded on Bruker Agilent 1100 / Esquire HCT PLUS (Bruker autoflex III smartbean for TOF-MS). The ^1H NMR was recorded on Bruker AVAEC-400(MHz) NMR spectrometer in CDCl_3 or DMSO using TMS as the internal standard. IR spectra was taken on a Nicolet 6700 Fourier transform (FT) IR spectrometer with KBr pellets. UV-vis spectra was obtained from Thermo Helios- γ spectrometer. The fluorescence spectra was recorded on WGY-10 spectrofluorometer using CH_2Cl_2 as solvent. TG was examined on Netzsch TGA209F3. DSC was performed with Netzsch 204-F1 thermal analysis system(scanning rate $10^\circ\text{C}/\text{min}$). Optical texture was investigated on Olympus polarizing optical microscope. The X-ray diffraction patterns were measured by Bruker D8 ADVANCE. The cyclic voltammetry curves were obtained from CHI750A electrochemical workstation (Zhenhua Apparatus Co., Ltd, Shanghai) using CH_2Cl_2 as solvent and Ag/AgCl as reference electrode.

2. Experimentation section

Meso-tetra(4-methoxycarbonylphenyl)porphyrin (TCMPP)

Methyl 4-formylbenzoate (2.5g, 15.24mmol) and propionic acid (70ml) were added to a 150ml three-necked flask and heated to 80°C . The freshly distilled pyrrole(1ml, 14.41mmol, dissolved in 10ml propionic acid) was added into the flask dropwise and then the mixture was heated to 140°C . After refluxing for 1h, the solution was cooled

to room temperature and methanol(30ml) was added into the flask and put into the freezer for overnight. The solids were filtered out and then applied to silica gel column using CH_2Cl_2 as eluent. Meso-tetra(4-methoxycarbonylphenyl)porphyrin (TCMPP) was obtained and the yield was 30%.

MS (ESI): $m/z = 847.7$ $[\text{M}+\text{H}]^+$, calcd. for $\text{C}_{52}\text{H}_{38}\text{N}_4\text{O}_8$: 846.8; ^1H NMR (400 MHz, CDCl_3 , TMS) δ (ppm) = 8.92 (s, 8H, pyrrole ring), 8.17-8.25(d, 16H, $-\text{C}_6\text{H}_4$), 4.08(s, 12H, $-\text{CH}_3$), -2.90 (s, 2H, pyrrole NH); IR (KBr) ν (cm^{-1}): 3320, 2947, 2894, 1720, 1600, 1555, 1435, 963.

Meso-tetra(4-carboxylphenyl)porphyrin (TCPP)

TCMPP(0.4g, 0.47mmol), KOH solution(20ml, 5% mass ratio) and THF(70ml) were added to a 150ml round-bottom flask and refluxed for 24h. The reaction was monitored by thin-layer chromatography (TLC). THF was removed through rotary evaporator after the reaction was finished, and the mixture was carefully neutralized with dilute HCl solution to pH = 2-3. Washed the solid with distilled water for several times and obtained TCPP (0.33g, yield 89%).

MS (ESI): $m/z = 791.5$ $[\text{M}+\text{H}]^+$, calcd. for $\text{C}_{48}\text{H}_{30}\text{N}_4\text{O}_8$: 790.7; ^1H NMR (400 MHz, DMSO, TMS) δ (ppm) = 8.82 (s, 8H, pyrrole ring), 8.25-8.38(d, 16H, $-\text{C}_6\text{H}_4$), -2.90 (s, 2H, pyrrole NH); IR (KBr) ν (cm^{-1}) = 3635, 3315, 1710, 1605, 1475, 1401, 963

5,10,15,20-tetra(4-(*N*-stearyl-carboxamide)phenyl)porphyrin (4NC₁₈-TPP)

A mixture of TCPP(0.1g, 0.126mmol), SOCl₂(5ml) and CH₂ClCH₂Cl(30ml) were refluxed for 8h under nitrogen atmosphere in a 100ml three-necked flask. The excess SOCl₂ and solvent were removed under reduced pressure after the reaction was finished. The remanent solid was dissolved in CH₂Cl₂(40ml) and triethylamine(2ml) and then n-octadecanamine was added into the flask. The mixture was stirred in ice water for 3h and then at room temperature for 12h under the nitrogen protection. The solvent was removed and the residue was purified by silica gel column chromatography using CHCl₃ as eluent. The first band was collected and condensed to obtain the target product 4NC₁₈-TPP (79.50mg, 35%).

TOF-MS: 1796.245, calcd. for C₁₂₀H₁₇₈N₈O₄: 1796.400; ¹H NMR(400MHz, CDCl₃, TMS), δ(ppm) = -2.81(s, 2H, pyrrole NH), 0.85-0.88(t, 12H, -CH₃), 1.25-1.54(m, 128H, alkyl CH₂), 3.63-3.65(t, 8H, -NH-CH₂^{*}-), 6.40-6.43(t, 4H, -CO-NH-), 8.14-8.28(d, 16H, -C₆H₄), 8.81(s, 8H, pyrrole ring). IR(KBr), ν (cm⁻¹) = 3306(ν amide N-H and pyrrole N-H), 2918, 2850(ν C-H), 1636(ν C=O), 1539(β, amide N-H), 966(β, pyrrole N-H).

3. MS, ^1H NMR and IR Spectra of the Products

Figure S1. Mass spectrum of TCMPP

Figure S2. Mass spectrum of TCPP

Figure S3. Time of flight-mass spectrum of 4NC₈-TPP

Figure S4. Time of flight-mass spectrum of 4NC₁₈-TPP

Figure S5. ^1H NMR Spectrum of TCMPP (400 MHz, CDCl_3 , ppm)

Figure S6. ^1H NMR Spectrum of TCPP (400 MHz, DMSO, ppm)

Figure S7. ^1H NMR Spectrum of 4NC₈-TPP (400 MHz, CDCl₃, ppm)

Figure S8. ^1H NMR Spectrum of 4NC₁₈-TPP (400 MHz, CDCl₃, ppm)

Figure S9. FTIR Spectra for TCMPP

Figure S10. FTIR Spectra for TCPP

Figure S11. FTIR Spectra for 4NC₈-TPP

Figure S12. FTIR Spectra for 4NC₁₈-TPP