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Circularly Polarized Absorption Property of Tetra-4[4'-(2-methylbutoxy)benzoyloxy]phenyl Porphyrin by Introducing Optical Pendant Groups

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Abstract: Tetra-4[4'-(2-methylbutoxy)benzoyloxy]phenyl porphyrin [T(MBBP)P] has been synthesized and its solid film has strong CD absorption effect.

Keywords: T(MBBP)P, circularly polarized absorption, CD, synthesis.

Circularly polarized luminescent(CPL) materials possess special dissymmetric optical property, *i.e.* luminescent light having different intensities for left (L) and right(R) circularly polarized components. Recently, these materials have been applied in colour-image projection, stereoscopic displays and light-emitting diodes(LEDS)[1-7]. We have synthesized a new porphyrin derivative, tetra-4[4'-(2-methylbutoxy)benzoyloxy] phenyl porphyrin [T(MBBP)P], by introducing a chiral group, which possesses strong circularly polarized absorption and is expected to be a new luminescent material.

T(MBBP)P was synthesized by esterification of tetra-(4-hydroxyphenyl) porphyrin [T(4-HP)P] and 4-(2-methylbutoxy)benzoyl chloride which was synthesized early in our laboratory[8](**Scheme1**). Hence, [T(4-HP)P] 0.42 g(0.62 mmol) and 4-(2-methyl-butoxy)benzoyl chloride 2.24 g(10 mmol) were added to 100 mL benzene contained l mL triethylamine as catalyst, refluxed for 8-10 h under N_2 atmosphere. The mixture was separated on silica gel column with chloroform and ethyl acetate (10: 0.2 v/v) as eluent and was further purified by silica gel column with benzene-chloroform-ethyl acetate (8: 2: 0.15 v/v) as eluent. Yield of T(MBBP)P was 25%. H^1 NMR: δ_H($CDCl_3$, ppm), 8.95(s, 8H, β-pyrrole), 7.02-8.34(m, 32H, Ar-H), 3.87-4.15 (m, 8H, OCH_2), 1.55-1.69(m, 4H, CH), 1.3-1.39(m, 8H, CH_2), 0.99(s, 12H, CH_3-CH), 0.94 (s, 12H, CH_3-CH_2), -2.77(s, 2H, N-H). FT-IR(KBr, cm^{-1}): 801, 1019, 1167(*p*-replaced benzene), 1257, (Ar-O), 1067(R-O), 1471(C-C, pyrrole), 1510, 1605(C=C), 1734(C=O)2924, 22871(C-H). MS(*m/z*): M+1, 1440. UV-Vis: λ_{max} (nm): 415, 448, 514, 553, 608, 660. Anal. Calcd. (found) C 76.77 (76.96), H 5.98 (5.91), N 3.89(3.64) .

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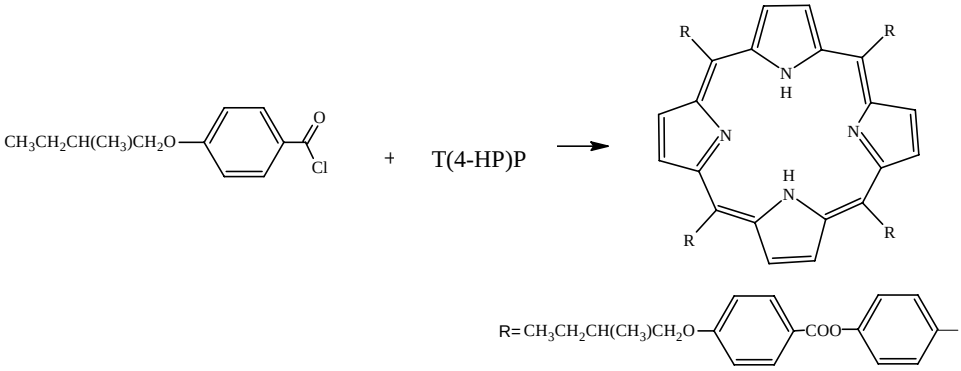
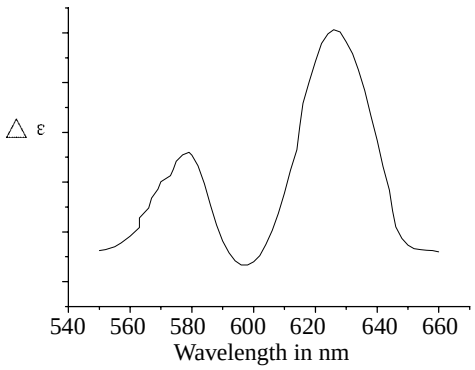
Scheme 1



Solid film was prepared through dropping chloroform solution of T(MBBP)P on quartz substrate. The solvent volatilized slowly at low temperature(0-10 ^{0}C), the thick of the film was about 10 μ m. We find that solid film has apparent CD absorption spectrum in 550-700 nm. But CD absorption has not been found when T(MBBP)P is in solution or in solid solution, formed by dissolving T(MBBP)P and PMMA (1: 10) in chloroform and then evaporating solvent (**Figure 1**).

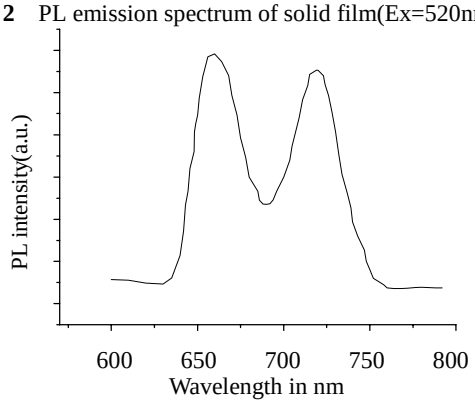
Figure 1 CD absorption spectrum of solid film



The origin of strong CD absorption is probably associated with the regiospecific substitution pattern of the chiral group on porphyrin ring, which results in the formation of small chiral aggregates[3], while these aggregstes are not existent in the solution and the solid solution.

Fluorescent emission spectrum of the solid film had been measured (**Figure 2**). Because its emissive wavelength is in the range of CD absorption wavelength, fluorescent emission spectrum of solid film probably possesses special CD spectrum. Furthermore, we have observed that the melting point range(267-321C^0) of T(MBBP)P has widened because of big plate ring of porphyrin and symmetric and flexible side chains in T(MBBP)P. We proposed that T(MBBP)P possesses the character of the plate liquid crystal. Further research work is progressing.

Figure 2 PL emission spectrum of solid film(Ex=520nm)



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