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Synthesis and solvent-dependent photochromic reactions of porphyrin–spiropyran hybrid compounds



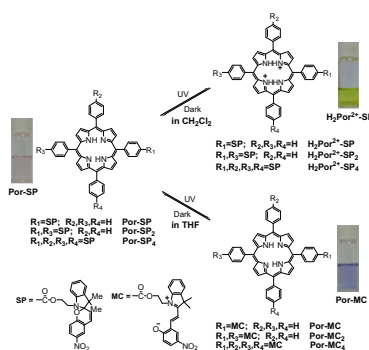
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HIGHLIGHTS

- Three hybrid compounds Por–SP, Por–SP₂, Por–SP₄ have been prepared.
- UV irradiation in CH₂Cl₂ and THF resulted in different solution colour.
- In dichloromethane, photoinduced protonation and reverse thermal deprotonation occurred.
- In THF, photoinduced ring-opening and reverse thermal ring-closing reaction occurred.

GRAPHICAL ABSTRACT



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ABSTRACT

Porphyrin(Por)–spiropyran(SP) hybrid compounds, including Por–SP dyad, Por–SP₂ triad, and Por–SP₄ pentad, were prepared and characterized by ¹H NMR, MALDI-TOF MS and UV–Vis spectroscopies. Upon 350 nm UV irradiation of Por–SP_n (*n* = 1, 2, 4) in dichloromethane, unusual red-shifted absorption spectra were observed with the colour change from pink into green. Probably due to the protonation of core nitrogens in porphyrin ring, their absorption maxima in dichloromethane were shifted from 418 (Soret band), 515, 550, 590, 645 (four Q bands) nm into 450 and 665 nm. Also, fluorescence maxima were also shifted from 650 and 715 nm to 692 nm. In the other hands, upon irradiation with 350 nm UV light in THF, the colour changed from pink into violet and absorption band at 590 nm increased and the fluorescence spectra showed the decrease of 650 and 715 nm bands and increase of 600–640 nm band, due to the normal ring-opening reaction of spiropyran moiety into merocyanine. In the dark, original absorption and fluorescence spectra were recovered very slowly in dichloromethane, but quickly in THF. The reversible photochromic reactions of Por–SP_n (*n* = 1, 2, 4) in dichloromethane and THF were investigated by observing absorption and fluorescence spectral changes during UV irradiation or standing in the dark.

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Introduction

Porphyrin is one of most frequently employed photoactive molecules due to strong absorption in the range of sunlight, relatively long excited singlet state lifetimes, and good redox properties. Porphyrin excited singlet state generated by the light absorption undergoes energy or electron transfer to the neighboring

component. A number of artificial light-harvesting antenna, photo-induced electron transfer systems, and molecular energy storage devices, optoelectronic switches including porphyrin-based multicomponent compounds have been investigated for a long time [1–11].

Spiropyran (SP), nonpolar UV-absorbing form, is well-known photochromic compound accomplishing reversible molecular structural changes to merocyanine (MC), polar VIS-absorbing form, by the photochemical ring opening on UV irradiation. In turn, MC is reversed to SP by ring closure thermally or on visible light

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irradiation. Reversible photochromic SP-MC transformation is one of subjects of active research on optical memory and switch, on the basis of significant difference in polarity, excited state energy, or molecular geometry between two forms [12–22].

Incorporating photochromic units into porphyrin-based multi-component compounds is expected to control on–off switching of photoinduced energy or electron transfer. If the excited singlet state energy of porphyrin lies between the excited singlet state energies of two isomers of these photochromic compounds, light-controlled quenching of the excited singlet state of porphyrin could be possible. Therefore, various multicomponent systems containing both porphyrin and photochromic compound such as azobenzene [23–25], spiropyran [26], dithienylethene [27], dihydropyrene [28], or dihydroindolizine [29,30] have been reported with their light-controlled on–off switching of photoinduced processes.

Photoswitched singlet energy transfer of porphyrin–spiropyran dyad has been reported. However, the photochromic reactions of porphyrin–spiropyran conjugates containing multiple photochromic components have not yet been systematically investigated.

In this paper, we report how photochromic reactions are affected by solvents and the number of attached spiropyran units in porphyrin(Por)–spiropyran(SP) hybrid compounds.

Experimental

Materials

All reagents were commercially available and used as received. The reagents were purchased from Sigma–Aldrich. Solvents were dried according to literature procedures.¹ Solvents for chromatography (ethyl acetate and hexane) were reagent grade and used without further purification. TLC was performed on Merck Silica Gel 60 F254 glass plates and developed by UV light. Column chromatography was performed on Merck Silica Gel 60 (70–230 mesh, ASTM). Por–CO₂H (5-(4-carboxyphenyl)-10,15,20-triphenylporphyrin), Por–(CO₂H)₂ (5,15-di-(4-carboxyphenyl)-10,20-diphenylporphyrin), and SP-OH were synthesized following the reported procedure. Por–(CO₂H)₄ (5,10,15,20-tetra-(4-carboxyphenyl)-porphyrin) was purchased from Sigma–Aldrich.

Spectroscopic measurements

¹H NMR spectra were recorded on Bruker Avance 400 NMR spectrometer. MALDI-TOF mass spectrum was recorded on an Applied Biosystems Voyager-DE STR System 4407 mass spectrometer using 2,5-dihydroxybenzoic acid in THF as matrix. UV–Vis absorption spectra were recorded using a quartz cuvette in a Shimadzu UV-2401PC spectrophotometer. Steady-state fluorescence spectra were measured on a SLM-Aminco AB2 luminescence spectrophotometer. The excitation wavelength for the emission spectra was fixed at 360 nm or 515 nm for free base porphyrin derivatives and 550 nm for zinc porphyrin derivatives. Photoirradiation was carried out in a Rayonet RPR 100 photochemical reactor equipped with Southern Ultraviolet 3500 Å lamps using Pyrex reaction tube in dichloromethane or tetrahydrofuran solution. Reaction progress of photochromic reaction on UV irradiation and reverse thermal reaction in the dark was monitored by change of absorption and fluorescence spectra. UV–Vis absorption and fluorescence spectra were measured with 5×10^{-6} M solution.

Synthesis

Por–SP: Por–CO₂H (20 mg, 0.03 mmol) was dissolved in DMF/CH₂Cl₂ (3/2, v/v) (5 mL) and then EDC(1-[3-(dimethylamino)propyl]-3-ethyl carbodiimide hydrochloride, 10 mg, 0.05 mmol),

and DMAP(4-(dimethylamino)pyridine, 6 mg, 0.05 mmol) were added successively. The reaction mixture was stirred at room temperature for 30 min under N₂ flow. SP-OH (14 mg, 0.04 mmol) was then added and the reaction mixture was stirred at room temperature for 24 h. The solvents were removed in *vacuo* and then CH₂Cl₂ (20 mL) and H₂O (20 mL) were added to the resulting residue. The CH₂Cl₂ layer was separated and successively washed with aqueous saturated NaCl solution and aqueous saturated NaHCO₃ solution. The CH₂Cl₂ layer was dried with anhydrous Na₂SO₄ and concentrated under reduced pressure and the resulting residue was purified by silica gel column chromatography using hexane/ethyl acetate (4/1, v/v) as the eluent to give **Por–SP**: (13 mg, yield 43%) as a purple solid: ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.89 (6H, t, $J = 8.05$ Hz, pyrrole), 8.79 (2H, d, $J = 4.68$ Hz, pyrrole), 8.42 (2H, d, $J = 8.24$ Hz, benzoate), 8.32 (2H, d, $J = 8.21$ Hz, benzoate), 8.10–8.08 (2H, m, benzene), 7.84–7.76 (9H, m, phenyl), 7.34–7.32 (1H, m, benzene), 7.17 (1H, d, $J = 1.82$ Hz, benzene), 7.06–6.93 (3H, m, benzene and –CHCH–benzene), 6.88 (1H, d, $J = 9.22$ Hz, benzene), 6.06 (1H, d, $J = 4.26$ Hz, –CHCH–benzene), 4.17–4.12 (2H, m, –CH₂CH₂–OH), 3.86–3.65 (2H, m, –CH₂CH₂–OH), 1.37 (3H, s, methyl), 1.31 (3H, s, methyl), –2.88 (2H, s, pyrrole–NH); MALDI-TOF MS m/z calculated for C₆₅H₄₈N₆O₅ 992.37, found 993.34 [M]⁺.

Por–SP₂: Por–(CO₂H)₂ (20 mg, 0.03 mmol) was dissolved in DMF/CH₂Cl₂ (3/3, v/v) (6 mL) and then EDC(20 mg, 0.1 mmol), and DMAP(13 mg, 0.1 mmol) were added successively. The reaction mixture was stirred at room temperature for 30 min under N₂ flow. SP-OH(14 mg, 0.04 mmol) dissolved in CH₂Cl₂ (6 mL) was then added and the reaction mixture was stirred at room temperature for 65 h. The next steps were accomplished according to the procedure described above. The solvents were removed in *vacuo* and then CH₂Cl₂ (20 mL) and H₂O (20 mL) were added to the resulting residue. The CH₂Cl₂ layer was separated and successively washed with aqueous saturated NaCl solution and aqueous saturated NaHCO₃ solution. The CH₂Cl₂ layer was dried with anhydrous Na₂SO₄ and concentrated under reduced pressure and the resulting residue was purified by silica gel column chromatography using hexane/ethyl acetate (3/1, v/v) as the eluent to give **Por–SP₂** (16 mg, yield 39%) as a purple solid: ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.90 (4H, d, $J = 4.28$ Hz, pyrrole), 8.80 (4H, d, $J = 4.87$ Hz, pyrrole), 8.42 (4H, d, $J = 8.18$ Hz, benzoate), 8.32 (4H, d, $J = 8.13$ Hz, benzoate), 8.24 (4H, d, $J = 8.13$ Hz, phenyl), 8.12–8.00 (4H, m, benzene), 7.83–7.77 (6H, m, phenyl), 7.34–7.33 (2H, m, benzene), 7.18 (2H, d, $J = 7.25$ Hz, benzene), 7.04–6.93 (6H, m, benzene and –CHCH–benzene), 6.85 (2H, d, $J = 9.40$ Hz, benzene), 6.05 (2H, d, $J = 10.35$ Hz, –CHCH–benzene), 4.18–4.09 (4H, m, –CH₂CH₂–OH), 3.86–3.64 (4H, m, –CH₂CH₂–OH), 1.36 (6H, s, methyl), 1.28 (6H, s, methyl), –2.80 (2H, s, pyrrole–NH); MALDI-TOF MS m/z calculated for C₈₆H₆₆N₈O₁₀ 1370.49, found 1393.43 [M+Na]⁺.

Por–SP₄: Por–(CO₂H)₄ (20 mg, 0.025 mmol) was dissolved in DMF/CH₂Cl₂ (3/5, v/v) (16 mL) and then EDC(58 mg, 0.3 mmol), and DMAP(37 mg, 0.3 mmol) were added successively. The reaction mixture was stirred at room temperature for 30 min under N₂ flow. SP-OH (10 mg, 0.15 mmol) dissolved in CH₂Cl₂ (10 mL) was then added and the reaction mixture was stirred at room temperature for 6 days. The next steps were accomplished according to the procedure described above. The solvents were removed in *vacuo* and then CH₂Cl₂ (20 mL) and H₂O (20 mL) were added to the resulting residue. The CH₂Cl₂ layer was separated and successively washed with aqueous saturated NaCl solution and aqueous saturated NaHCO₃ solution. The CH₂Cl₂ layer was dried with anhydrous Na₂SO₄ and concentrated under reduced pressure and the resulting residue was purified by silica gel column chromatography using CH₂Cl₂/ethyl acetate (50/1, v/v) as the eluent to give **Por–(SP)₄** (14 mg, yield 27%) as a purple solid: ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.84 (8H, d, $J = 12.3$ Hz, pyrrole), 8.42 (8H, d, $J = 8.22$ Hz, benzoate), 8.31 (8H, d, $J = 13.38$ Hz, benzoate), 8.10–8.07 (8H, m,

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