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Mild synthesis and photophysical properties of symmetrically substituted diketopyrrolopyrrole derivatives

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ABSTRACT

A series of symmetrically substituted diketopyrrolopyrrole derivatives were synthesized under mild conditions in good yields. All of the diketopyrrolopyrroles were characterized by ^{1}H and ^{13}C NMR, ultraviolet–visible and fluorescence spectroscopy, high resolution mass spectrometry and elemental analysis. The maximum absorption and emission bands showed gradual red-shift with the increase in electron donating strength of the 3,6-substituent. In addition, the optical properties of 4,4′-(2,5-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-*c*]pyrrole-1,4-diyl)dibenzoic acid and 3,6-bis(4-hydroxyphenyl)-2,5-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione were investigated under alkaline conditions. The results demonstrated that 3,6-bis(4-hydroxyphenyl)-2,5-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione could be employed as an acid–base indicator. These diketopyrrolopyrroles derivatives have potential application in the synthesis of novel organic optoelectronic materials and in biological systems as a consequence of the increased water solubility.

1. Introduction

1,4-Diketo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole (DPP) derives from a class of brilliant red, strongly fluorescent high-performance pigments that have good light-resistant, weather-resistant, and solvent-resistant properties. DPP derivatives have advantageous optical properties, such as strong absorption and emission in the visible region, high photostability, large Stokes shift, and with a significant two-photon absorption cross section [1–7]. Recently, significant effort has been made to apply DPP based materials in small molecular and polymer solar cells (PSCs), organic field effect transistors (OFETs), and organic light-emitting diodes (OLEDs) [8–12]. This work was recently reviewed by H. Tian et al. [13].

In this regard, much effort has been made to expand the scope of DPP-based chromophores for designing colorful dyes and functional materials [14–23]. Herein mild synthesis of novel dyes were reported, which were functionalized in the 3,6-position of DPP with CHO, COOH, OH, CH_2OH groups. Furthermore photophysical and chemical properties of diketopyrrolopyrrole derivatives were investigated. Moreover, these functionalized DPP derivatives have potential application in the synthesis of novel organic optoelectronic materials and in biology as these chains induce water solubility.

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2. Materials and methods

2.1. Experimental

2.1.1. General

Unless otherwise stated, reagents were commercially obtained and used without further purification. Reactions were monitored by TLC. Flash chromatography separations were carried out using silica gel (200–300 mesh). ^{1}H NMR and ^{13}C NMR spectra were collected on a Bruker Avance DPS-300 spectrometer using $CDCl_3$ or DMSO-d_6 as solvent and tetra-methylsilane as an internal reference. Mass spectrometry was performed with Bruker Biflex III MALDI-TOF (both positive and negative ion reflector mode). Absorption spectra were measured on a Thermo UV–Vis spectrophotometer. Fluorescence spectra were measured on a Thermo fluorescence spectrophotometer. Both excitation and emission slit widths were 2.5 nm.

2.2. Synthesis

2.2.1. Synthesis of compound 3,6-bis(4-(1,3-dioxolan-2-yl)phenyl) pyrrolo[3,4-c]-pyrrole-1,4(2H,5H)-dione (**1**)

Sodium (2.30 g, 100 mmol) was dissolved in *t*-amyl alcohol (50 mL) at 90 °C over 1 h with catalytic amount of $FeCl_3$, then the solution was cooled to 50 °C, 4-(1,3-dioxolan-2-yl)benzonitrile

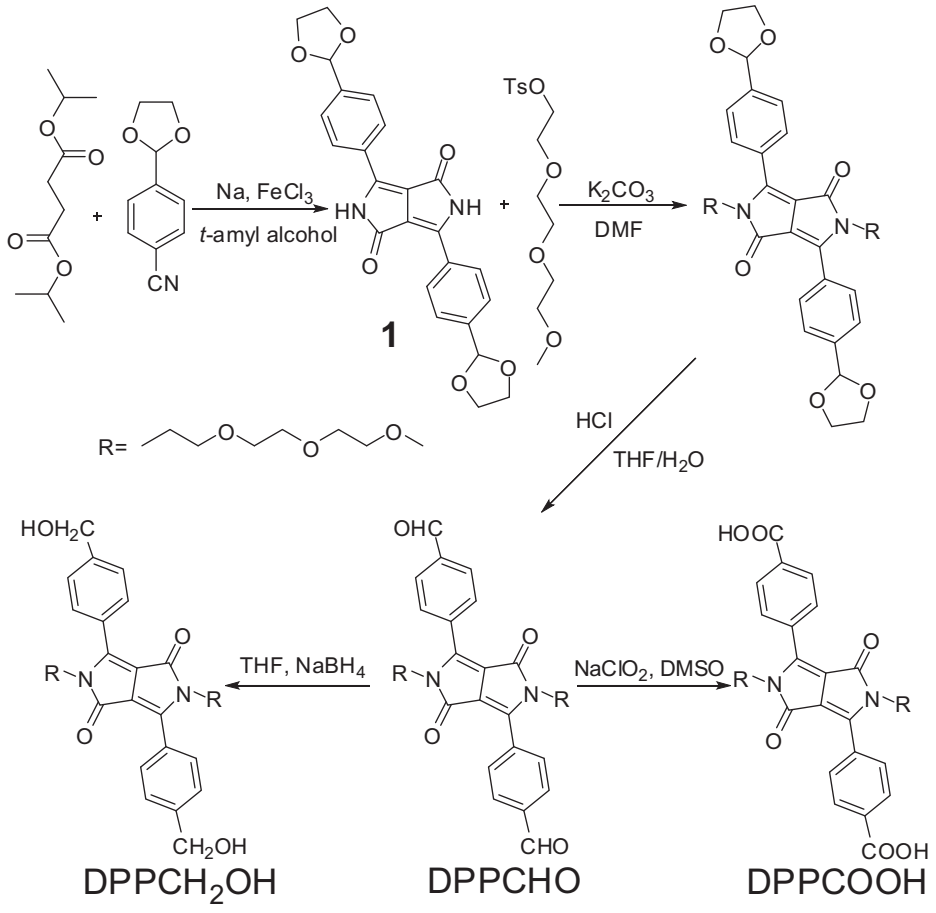
(prepared by reference 24) (7.00 g, 40 mmol) was added. The mixture was heated to 90 °C, diisopropyl succinate (4.00 g, 40 mmol) in *t*-amyl alcohol (20 mL) was added over 2 h. Subsequently, the resulting suspension was kept for 3 h at 120 °C, and then cooled to room temperature. Glacial acetic acid was slowly added till pH was 7.0, followed by methanol and water (1:2, v:v, 100 mL) added, the mixture was heated under reflux for 2 h. After cooling filtration and dried, a bluish-red solid was obtained (4.00 g, 30%). The product was used without further purification [15].

*2.2.2. Synthesis of compound 4,4′-(2,5-bis(2-(2-(2-methoxyethoxy) ethoxy)ethyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)dibenzaldehyde (**DPPCH O**)*

1 (0.22 g, 0.5 mmol), K_2CO_3 (0.27 g, 2 mmol) and DMF (50 mL) were added into a three-necked flask. After 30 min at 120 °C, 2-(2-(2-methoxyethoxy)ethoxy)ethyl-4-methylbenzenesulfonate (4.00 g, 10 mmol) was added slowly, the mixture was stirring at 120 °C for 2 h. After the reaction stopped, water (50 mL) was added, the mixture was extracted with ethyl acetate (2 × 50 mL). The solvent was dried with Na_2SO_4 and evaporated under vacuum. The mixture (used without further purification) together with THF (50 mL) and HCl (2.0 mol/L, 2.5 mL), were stirred at 60 °C for 1 h. The solvent was removed to give an orange solid, which was purified by column chromatography (CH_2Cl_2/CH_3OH = 50/1) to give the compound DPPCHO (0.21 g, 65%), mp: 161–165 °C; IR (KBr) *v* 3445, 2881, 2879, 1700, 1664, 1596, 1558, 1384, 1361, 1217, 1105, 1086, 1036, 850,738 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 3.35 (s, 6H), 3.51 (m, 4H), 3.56 (m, 12H), 3.76 (t, *J* = 5.2 Hz, 4H), 3.94 (t, *J* = 5.2 Hz, 4H), 8.04 (d, *J* = 8.4 Hz, 4H), 8.22 (d, *J* = 8.4 Hz, 4H), 10.09 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 42.5, 59.1, 68.8, 70.5, 70.5, 70.6, 71.9, 110.8, 129.9, 130.1, 133.2, 137.6, 148.4, 162.6, 191.4 ppm; HRMS (TOF-ESI$^+$): *m*/*z*: calcd for $C_{34}H_{40}N_2O_{10}^+$: 636.2683; calcd for $C_{34}H_{41}N_2O_{10}^+$: 637.2761 [M + H^+]; found: 637.2758; Anal. Calcd. for $C_{34}H_{40}N_2O_{10}$: C, 64.14; H, 6.33; N, 4.40. Found: C, 64.23; H, 6.05; N, 4.17.

*2.2.3. Synthesis of compound 4,4′-(2,5-bis(2-(2-(2-methoxyethoxy) ethoxy)ethyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)dibenzoic acid (**DPPCO OH**)*

$NaClO_2$ (0.90 g, 10 mmol), H_2O (5 mL), NaH_2PO_4 (0.16 g), DPPCHO (0.63 g, 1.0 mmol) were added into a flask with DMSO (30 mL) and water (2 mL). The mixture was kept overnight at room temperature, then 5% $NaHCO_3$ aqueous solution was added, the aqueous phase was acidified with 10 N aqueous HCl and extracted with ethyl acetate (3 × 50 mL). The solvent was dried with Na_2SO_4 and evaporated under vacuum. The mixture was purified by column chromatography (CH_2Cl_2/CH_3OH = 20/1) to give the compound DPPCOOH (0.55 g, 80%), mp: 199–205 °C, IR (KBr) *v* 3433, 2920, 2883, 1706, 1673, 1600, 1380, 1184, 1094, 1044, 848, 743, 678 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3/CD_3OD$): 3.35 (s, 6H), 3.51 (m, 4H), 3.55 (m, 12H), 3.72 (t, *J* = 5.2 Hz, 4H), 3.94 (t, *J* = 5.2 Hz, 4H), 8.05 (d, *J* = 8.4 Hz, 4H), 8.19 (d, *J* = 8.4 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 42.1, 58.8, 68.6, 70.3, 70.4, 71.7, 110.3, 129.2, 130.1, 131.81, 132.6, 148.7, 162.7, 167.8 ppm; HRMS (TOF-ESI$^+$): *m*/*z*: calcd for $C_{34}H_{40}N_2O_{12}^+$: 668.2581; calcd for $C_{34}H_{41}N_2O_{12}^+$: 669.2659 [M + H^+]; found: 669.2667; Anal. Calcd. for $C_{34}H_{40}N_2O_{12}$: C, 61.07; H, 6.03; N, 4.19. Found: C, 61.43; H, 6.25; N, 4.03.



Scheme 1. The synthetic routes to compounds DPPCHO, $DPPCH_2OH$, DPPCOOH.