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Palladium(0) catalyzed 2,2'-bipyrrole syntheses

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Abstract

Several 2-iodopyrroles are used in Pd(0) catalyzed homocoupling reactions at room temperature in the presence of water to efficiently synthesize 2,2'-bipyrroles. These 2,2'-bipyrroles are strongly luminous materials and have high fluorescence quantum yields.

Keywords

bipyrrole; homocoupling; iodopyrrole; palladium

INTRODUCTION

The bipyrrole motif occurs in natural products, pigments, and in porphyrin mimics. They are also well-known common components in molecular recognition and self-assembly processes [1]. Recently, bipyrrole-containing macrocycles have attracted increased attention as therapeutic agents in combination with visible light for the treatment of tumors, especially in connection with extended pyrrole systems [2] such as porphycenes [3, 4] and sapphyrins [5]. However, a key potential synthetic precursor for these compounds, namely 2,2'-bipyrroles, have only limited synthetic methods available [4–7].

The Ullmann coupling and oxidative coupling are the two most common synthetic methods [4–7]: Ullmann coupling has found broad synthetic application in the generation of biaryls [8a] and bipyrroles [4, 5, 7]; oxidative coupling has been used for the generation of 2,2'-bipyrroles possessing electron-rich substituents [6]. However, only a limited array of 2,2'-bipyrroles can be accessed using these two methods due, but not limited to, the harsh reaction conditions: Ullmann coupling typically requires high temperature ($T \geq 200\text{ }^{\circ}\text{C}$) [8b], stoichiometric amounts of the copper catalyst, and specific requirements for successful substrates, *e.g.* at least one electron-withdrawing group. Oxidative coupling [6] requires substoichiometric amounts of the Pd(II) catalyst, special substrates, pyrrolinones or bipyrroles, and tedious purification procedures associated with poor regioselectivity of the reaction.

Recently, several improvements had been made in 2,2'-bipyrrole syntheses [6, 7, 8d, 8e], but each has its own limitations. Kita [6] and coworker used PIFA and TMSBr as assisting reagents to improve the oxidative coupling, but the poor regioselectivity problem remains. Sessler [7a] and coworker protected the pyrrole nitrogen to improve the Ullmann coupling and Vogel [7b] further improved the method by substitution of DMF with toluene as a solvent; however, high temperatures are still required and some functional groups can not survive. Liebeskind [8c] and coworkers improved the Ullmann coupling by performing it at ambient temperature, but as the authors stated "the most noticeable limitation of this process is the lack of aromatic halide substrates not possessing a coordinating *ortho*-substituent".

As part of our efforts to improve the porphycene synthesis [9], an improved synthetic route for 2,2'-bipyrrole was developed. We were attracted to the wide usage of Pd catalysts in coupling reactions to form carbon-carbon bonds [10a-c], such as the Stille [10b], Suzuki [10c], Heck [10d], and Sonogashira [10e] couplings, and thus introduced the Pd(0) catalyzed homo-coupling reaction into 2,2'-bipyrrole syntheses. Although Pd-C has been previously used as a catalyst in the Ullmann coupling, phase-transfer reagents and 100 °C reflux conditions are required [10]. Inspired by recent improved syntheses of biaryls through Pd(0) catalyzed couplings at ambient temperature [11], our improved syntheses reduced the synthetic steps for most of the 5,5'-diformyl-2,2'-bipyrroles studied [12] by using Pd-C and zinc as co-catalyst with the presence of water. Considering the substituent array, and especially those at the 2- or 5-position of pyrroles, generally affect both the Ullmann and oxidative coupling reactions, the versatility of this reaction and the photo-physical properties of the resulting 2,2'-bipyrroles are now discussed in the present paper.

EXPERIMENTAL

General

Silica gel (32-63 μm) was used for flash column chromatography. All reactions were monitored by TLC using 0.25 mm silica gel plates with (60F-254) or without UV indicator. ^1H and ^{13}C NMR spectra were obtained on either a DPX-250 or a ARX-300 Bruker spectrometer. Chemical shifts (δ) are given in ppm relative to CDCl_3 as indicated in each spectra. Mass spectra were obtained on an Applied Biosystems QSTAR XL. All solvents (HPLC grade) were obtained from Fisher Scientific (Houston, TX) and used without further purification unless otherwise indicated. Acetone (reagent plus, phenol free, $\geq 99.5\%$) and toluene (HPLC grade) were purchased from Sigma-Aldrich. Palladium, 10% on activated carbon was purchased from Strem Chemicals. Zinc dust, <10 micro, 98+%, was purchased from Sigma-Aldrich and actived according to the literature [12]. Monopyrroles used to make 2-iodopyrroles were synthesized according to the literature [13]. UV-visible absorption spectra were recorded on a Hitachi U-3010 Spectrophotometer (190-1100 nm scan range). Fluorescence emission spectra were recorded on a Hitachi F-4600 FL Spectrophotometer. The slit widths were 2.5 nm and 5.0 nm for excitation and emission respectively. Fluorescent quantum yields were calculated using a secondary standard method by comparing the areas under the corrected emission spectrum of the test sample in various solvents with that of the standard. Dilute solutions ($0.01 < A < 0.05$) were used to minimize reabsorption effects and correction for the solvent refractive index was applied. Quinine sulfate in 5% H_2SO_4 solution ($\Phi_F = 0.56$) [14] was used as a fluorescence standard for the fluorescence quantum yield calculations according to the absorption of the test sample. Quantum yields were determined using the following equation [14]:

$$\Phi_x = \Phi_s (I_x/I_s) (A_s/A_x) (\eta_x/\eta_s) \quad (1)$$

where Φ_S is the reported quantum yield of the standard, I is the integrated emission spectra, A is the absorbance at the excitation wavelength and η is the refractive index of the solvent being used ($\eta = 1$ when the same solvent was used for both the test sample and the standard). Subscript X indicates the test sample, and subscript S the standard.

General procedure for the preparation of 2-iodopyrroles

2-iodopyrroles were obtained from successive debenzylation and iodination reactions of pyrrole esters. Debenzylation was performed using hydrogen and 6 mmol.% Pd-C as catalyst in freshly distilled dry THF. Before adding pyrrole, the catalyst was activated by stirring it under a hydrogen atmosphere for 20 min. After completion of the reaction, the mixture was passed through a Celite plug and washed with THF several times. After evaporation of the solvent under vacuum, the resulting pyrrole carboxylic acid was used directly for the iodination process, in a mixture of 1,2-dichloroethane and saturated aqueous NaHCO_3 under reflux with a mixture of I_2/KI as the iodination reagent. It usually took 1 h to complete the reaction. After cooling to room temperature, sodium thiosulfate was added in small portions before pouring the mixture into a separatory funnel. The organic layer was collected and the solvent was removed under vacuum. The resulting solid was purified by recrystallization from methanol.

Diethyl 3-(2-ethoxyethyl)-5-iodopyrrole-2,4-dicarboxylate (1a)[13c]—83% yield. mp 148–150 °C {lit [13c] mp 150 °C}. ^1H NMR (250 MHz, CDCl_3): δ , ppm 9.30 (s, 1H), 4.40–4.33 (m, 4H), 3.55–3.52 (m, 2H), 3.44–3.41 (m, 2H), 3.37 (s, 3H), 1.43–1.36 (m, 6H). ESI-MS: m/z calcd. for $\text{C}_{14}\text{H}_{20}\text{INO}_4$, 393.04, found: 392.90.

Benzyl 5-iodo-3,4-dimethylpyrrole-2-carboxylate (1c)[13d]—81% yield. mp 127–129 °C {lit [13d] mp 126–128 °C}. ^1H NMR (250 MHz, CDCl_3): δ , ppm 8.80 (s, 1H), 7.47–7.38 (m, 5H), 5.34 (s, 2H), 2.35 (s, 3H), 2.00 (s, 3H). ESI-MS: m/z calcd. for $[\text{C}_{14}\text{H}_{14}\text{INO}_2]$, 355.01, found: 355.10.

Benzyl 5-iodo-3-methyl-4-propylpyrrole-2-carboxylate (1e)[13b]—79% yield. mp 118–120 °C {lit [13b] mp 119–120 °C}. ^1H NMR (250 MHz, CDCl_3): δ , ppm 9.01 (s, 1H), 7.45–7.34 (m, 5H), 5.32 (s, 2H), 2.37–2.32 (m, 5H), 1.52–1.43 (m, 2H), 0.97–0.91 (m, 3H). ^{13}C NMR (250 MHz, CDCl_3): δ , ppm 160.77, 136.58, 131.23, 129.02, 128.66, 127.66, 123.82, 74.13, 66.33, 28.86, 23.84, 14.27, 11.40. ESI-MS: m/z calcd. for $[\text{C}_{16}\text{H}_{18}\text{INO}_2]$, 383.22, found: 383.29.

Benzyl 5-iodo-3-(2-methoxycarbonyl)ethyl-4-methylpyrrole-2-carboxylate (1f)[13a]—87% yield. mp 110–112 °C {lit [13a] mp 110–111 °C}. ^1H NMR (250 MHz, CDCl_3): δ , ppm 7.38 (m, 5H), 5.30 (s, 2H), 3.64 (s, 3H), 3.10–3.04 (m, 2H), 2.53–2.47 (m, 2H), 2.00 (s, 3H). ESI-MS: m/z calcd. for $[\text{C}_{17}\text{H}_{19}\text{INO}_2 + \text{Na}]^+$, 450.03, found: 449.97.

***tert*-butyl 3-ethyl-5-iodo-4-methylpyrrole-2-carboxylate (1g)[13c]**—77% yield. mp 105–107 °C {lit [13c] mp 105–107 °C}. ^1H NMR (250 MHz, CDCl_3): δ , ppm 9.49 (s, 1H), 3.68 (s, 3H), 2.54–2.47 (m, 2H), 1.97 (s, 3H), 1.56 (s, 9H). ESI-MS: m/z calcd. for $\text{C}_{14}\text{H}_{20}\text{INO}_4$, 393.04, found: 392.90.

General procedure for the reductive coupling of 2-iodopyrroles

Zinc metal was activated by washing with 3 M HCl. After filtering through filter paper and successive washing with water, ethanol, and diethyl ether, it was dried under vacuum. Pd-C (4 mmol.%) and activated Zn powder (1.5 mmol) were placed in a dry 50 mL round bottom flask. After removing air under vacuum, the flask was filled with argon. Then 2-iodopyrrole (0.5 mmol) was dissolved in 10 mL acetone or toluene, and added through a syringe into the

reaction flask. Finally, 10 mL distilled water was added into the reaction mixture before stirring at room temperature under argon. TLC was used to monitor the reaction. Upon the completion of the reaction, THF (20 mL) was added and the mixture was filtered through a plug of Celite. After removing the THF under vacuum, the mixture was poured into a separatory funnel and DCM (50 mL) was added. The organic layer was collected and dried under vacuum. The resulting solid was purified either by recrystallization from ethanol or by using column separation.

Diethyl 3,3',4,4'-tetramethyl-2,2'-bipyrrole-5,5'-dicarboxylate (2a)—After separating on a silica gel column using a mixture of ethyl acetate and hexane as eluting solvent, pure **2a** was obtained as a milk-white solid in 15% yield (13.3 mg, 0.04 mmol). ¹H NMR (250 MHz, CDCl₃): δ, ppm 8.97 (s, 2H), 4.34–4.25 (m, 4H), 2.31 (s, 6H), 2.05 (s, 6H), 1.38–1.32 (m, 6H). ¹³C NMR (250 MHz, CDCl₃): δ, ppm 161.70, 127.42, 124.55, 119.60, 119.25, 60.02, 14.47, 10.51, 9.87. MALDI-TOF MS: *m/z* calcd. for C₁₈H₂₄N₂O₄, 332.17, found: 332.34.

Tetraethyl 4,4'-di(2-ethoxyethyl)-2,2'-bipyrrole-3,3',5,5'-tetracarboxylate (2b)—After recrystallization from DCM/hexane and washing with hexane (2 × 2 mL), pure **2b** was obtained as a milk-white solid in 45% yield (59.0 mg, 0.11 mmol). ¹H NMR (250 MHz, CDCl₃): δ, ppm 9.42 (s, 2H), 4.49–4.37 (m, 8H), 3.54–3.48 (s, 8H), 3.38 (s, 6H), 1.47–1.40 (s, 12H). FAB MS: *m/z* calcd. for C₂₆H₃₆N₂O₁₀, 536.24, found: 536.30. MALDI-TOF MS: *m/z* calcd. for C₂₆H₃₆N₂O₁₀, 536.24, found: 536.41.

Dibenzyl 3,3',4,4'-tetramethyl-2,2'-bipyrrole-5,5'-dicarboxylate (2c)—After recrystallization from MeOH/DCM and washing with hexane (2 × 2 mL), pure **2c** was obtained as a milk-white solid in 76% yield (86.8 mg, 0.19 mmol). mp 218–20 °C. ¹H NMR (250 MHz, CDCl₃): δ, ppm 9.08 (s, 2H), 7.39–7.34 (m, 10 H), 5.25 (s, 4H), 2.31 (s, 6H), 2.02 (s, 6H). ¹³C NMR (250 MHz, CDCl₃): δ, ppm 161.42, 136.25, 128.51, 128.07, 128.03, 127.90, 124.90, 119.87, 119.00, 65.78, 10.67, 9.89. HRMS (ESI): *m/z* calcd. for C₂₈H₂₉N₂O₄ [M + H]⁺, 457.2127, found 457.2124.

Dibenzyl 3,3'-diethyl-4,4'-dimethyl-2,2'-bipyrrole-5,5'-dicarboxylate (2d)—After recrystallization from DCM/hexane and washing with hexane (2 × 2 mL), pure **2d** was obtained as a milk-white solid in 77% yield (92.2 mg, 0.19 mmol). ¹H NMR (400 MHz, CDCl₃): δ, ppm 9.65 (s, 2H), 7.98 (s, 10H), 5.85 (s, 2H), 3.06–2.94 (m, 10H), 1.65 (s, 6H). ¹³C NMR (300 MHz, CDCl₃): δ, ppm 161.35, 136.23, 128.50, 128.02, 127.08, 126.82, 124.18, 119.04, 65.74, 17.69, 15.42, 10.59. HRMS (ESI): *m/z* calcd. for C₃₀H₃₃N₂O₄ [M + H]⁺, 485.2440, found 485.2444.

Dibenzyl 4,4'-bis(2-methoxycarbonyl)ethyl-3,3'-dimethyl-2,2'-bipyrrole-5,5'-dicarboxylate (2e)—After recrystallization from DCM/hexane and washing with hexane (2 × 2 mL), pure **2e** was obtained as a milk-white solid in 48% yield (72.1 mg, 0.12 mmol). ¹H NMR (250 MHz, CDCl₃): δ, ppm 9.21 (s, 2H), 7.37–7.33 (m, 10H), 5.23 (s, 4H), 3.63 (s, 6H), 3.07–3.01 (m, 4H), 2.54–2.47 (m, 4H), 2.05–2.00 (m, 6H). ¹³C NMR (250 MHz, CDCl₃): δ, ppm 173.89, 161.28, 136.28, 130.82, 128.98, 128.75, 128.66, 125.30, 120.14, 119.45, 66.56, 51.91, 35.07, 21.11, 10.16. HRMS (ESI): *m/z* calcd. for C₃₄H₃₇N₂O₈ [M + H]⁺, 601.2550, found 601.2540.

Dibenzyl 4,4'-dimethyl-3,3'-dipropyl-2,2'-bipyrrole-5,5'-dicarboxylate (2f)—After recrystallizing from MeOH/DCM and washing with hexane (2 × 2 mL), pure **2f** was obtained as a milk-white solid in 52% yield (66.7 mg, 0.13 mmol). ¹H NMR (250 MHz, CDCl₃): δ, ppm 8.73 (s, 2H), 7.44–7.33 (m, 10H), 5.31 (s, 4H), 2.44–2.33 (m, 10H), 1.49–

1.39 (m, 4H), 0.89–0.83 (m, 6H). ^{13}C NMR (250 MHz, CDCl_3): δ , ppm 161.09, 136.24, 128.56, 128.13, 127.64, 124.85, 124.44, 118.90, 65.80, 29.70, 26.56, 24.07, 13.95, 10.65. HRMS (ESI): m/z calcd. for $\text{C}_{32}\text{H}_{37}\text{N}_2\text{O}_4$ $[\text{M} + \text{H}]^+$, 513.2753, found 513.2759.

Di-*tert*-butyl 4,4'-diethyl-3,3'-dimethyl-2,2'-bipyrrole-5,5'-dicarboxylate (2g)—

After separating by using a silica gel column eluted with ethyl acetate and hexane, pure **2g** was obtained as a milk-white solid in 32% yield (33.4 mg, 0.08 mmol). ^1H NMR (250 MHz, CDCl_3): δ , ppm 8.66 (s, 2H), 2.81–2.72 (m, 4H), 2.05 (s, 6H), 1.58 (s, 18H), 1.19–1.13 (m, 6H). ^{13}C NMR (250 MHz, CDCl_3): δ , ppm 161.37, 133.51, 124.49, 120.30, 118.95, 81.10, 28.85, 18.84, 15.52, 10.08. HRMS (ESI): m/z calcd. for $\text{C}_{24}\text{H}_{37}\text{N}_2\text{O}_4$ $[\text{M} + \text{H}]^+$, 417.2753, found 417.2737.

Di-*tert*-butyl 4,4'-bis(2-methoxycarbonyl)ethyl-3,3'-dimethyl-2,2'-bipyrrole-5,5'-dicarboxylate (2h)—

After separating by using a silica gel column eluted with ethyl acetate and hexane, pure **2h** was obtained as a milk-white solid in 34% (45.3 mg, 0.09 mmol). ^1H NMR (250 MHz, CDCl_3): δ , ppm 8.75 (s, 2H), 3.67 (s, 6H), 3.08–3.01 (m, 2H), 2.60–2.54 (m, 2H), 2.05 (s, 6H), 1.56 (s, 18H). ^{13}C NMR (250 MHz, CDCl_3): δ , ppm 173.59, 160.66, 128.92, 123.98, 120.55, 119.12, 81.12, 51.48, 34.90, 29.67, 20.77, 9.68. HRMS (ESI): m/z calcd. for $\text{C}_{28}\text{H}_{41}\text{N}_2\text{O}_8$ $[\text{M} + \text{H}]^+$, 533.2862, found 533.2854.

X-ray crystallographic data

For **2c**: $\text{C}_{28}\text{H}_{28}\text{N}_2\text{O}_4$, triclinic space group P-1, $a = 9.4902(12)$, $b = 10.4909(15)$, $c = 12.485(2)$ Å, $\alpha = 75.282(7)^\circ$, $\beta = 85.399(8)^\circ$, $\gamma = 79.163(8)^\circ$, $V = 1180.1(3)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.285$ g cm⁻³, $\mu(\text{MoK}\alpha) = 0.086$ mm⁻¹, $R = 0.083$ for 3940 data with $\text{Fo}^2 > 2\sigma(\text{Fo}^2)$ of 4658 unique data and 380 refined parameters. A total of 26,411 data was collected at $T = 90.0(5)$ K to $\theta = 26.1^\circ$ with MoK α radiation ($\lambda = 0.71073$ Å) on a Nonius KappaCCD diffractometer, using a colorless crystal of dimensions $0.32 \times 0.23 \times 0.10$ mm. Refinement was by full-matrix least squares using SHELXL, with H atoms in idealized positions, except for NH hydrogen atoms, which were located by difference maps and their positions refined. Both phenyl groups are rotationally disordered, each having a conformer with 63% occupancy and another with occupancy 37%.

Crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC) under deposition number CCDC 817869. Copies can be obtained on request, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033 or deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

2-iodopyrroles **1a–h** were synthesized from monopyrroles [13] in gram scale using literature procedures [15], from which the desired 2,2'-bipyrroles were synthesized based on a Pd(0) catalyzed homocoupling reaction under argon (Table 1). Pd-C and zinc metal were used as co-catalysts, a mixture of acetone/water was used as solvent and the product yields are summarized in Table 1. Substituents, especially those adjacent to the pyrrole nitrogen atom, greatly affected the coupling reaction: 2-iodopyrroles **1c–f** ($\text{R}^3 = \text{PhCH}_2\text{O}_2\text{C}$) gave the highest yields of the desired 2,2'-bipyrroles (**2c–f**) while the other 2-iodopyrroles (**1a–b** and **1g–h**) gave a lower yield of 2,2'-bipyrrole with mainly the dehalogenated pyrrole (such as **3b**) as a by-product.

During an effort to improve the yields of (**2a–b**) and (**2g–h**), the solvent was found to play an important role in the coupling reaction. When a mixture of toluene/water was used as solvent (Table 2), the major product from the 2-iodopyrrole (**1b**) coupling changed from the

dehalogenated pyrrole (**3b**) to the desired 2,2'-bipyrrole (**2b**). Benzene has been reported to stabilize the Pd(II) intermediate during the coupling, thus it is also possible for the phenyl group of the 2-iodopyrroles benzyl esters to stabilize the Pd(0) intermediate in our system [16]: 2-iodopyrroles (**1c–f**) ($R^3 = \text{PhCH}_2\text{O}_2\text{C}$) most likely stabilized the Pd(0) intermediate, and thus higher yields were obtained. Among those 2-iodopyrroles with a $\text{PhCH}_2\text{O}_2\text{C}$ attached at the 5-position, (**1e**) gave a relatively low yield, possibly due to steric hindrance from the 3-propyl group of the 2-iodopyrrole.

It is also worth mentioning that water plays important roles in the coupling reaction. As shown in Table 2, when no water was added, the coupling of 2-iodopyrrole (**1b**) gave no product, and **1b** was recovered quantitatively even when the reaction time was extended to 4 d. However, after adding 0.1% water into the reaction mixture, within several hours most of **1b** was consumed: in the acetone system, most of **1b** was converted into **2b** within 2 h. In toluene, the yield of **2b** was increased from 5% to 45% within 6 h. However, in a toluene/water system, the conversion rate of **1b** was lower, with only 50% conversion being achieved. Since the completion of the Ullmann coupling for the generation of **2b** requires more than two days, extending the reaction time was expected to be helpful for increasing the conversion of **1b** in toluene/water. However, little improvement was observed even when the reaction time was extended to 2 d. Water has been reported [17] to be able to initiate or promote room temperature reactivity, possibly by decreasing of the reaction barrier. To test our hypothesis regarding toluene, toluene/water was also used for **1a–h**, as shown in Table 3.

Similar to the coupling results with **1b**, substitution of acetone with toluene improved the coupling yields of 2-iodopyrroles (**1a–b**) and (**1g–h**) only from low to modest: 4% to 15% for **1a**, 5% to 45% for **1b**, 7% to 32% for **1g** and 12% to 34% for **1h**, with little change being observed for **1c–f**. But the reaction became slow and the conversion rate of 2-iodopyrrole was lower in toluene compared with those in acetone. Thus for those 2-iodopyrroles with $\text{PhCH}_2\text{O}_2\text{C}$ at the 5-position, the mixture of acetone/water was shown to be more efficient than toluene/water. The X-ray structure of 2,2'-bipyrrole **2c** is shown in Fig. 1. The two pyrrole rings are not coplanar, but there is a twist about the central C–C bond of the molecule. The N1–C4–C5–N2 torsion angle is $-56.7(4)^\circ$. The ester carbonyl O atoms are nearly eclipsed with pyrrole N, N–C–C=O torsion angles being $3.2(4)$ and $4.9(4)^\circ$. The N–H and C=O groups form intermolecular hydrogen bonds in cyclic pairs about inversion centers, the N...O distances being 2.831(3) and 2.936(3) Å.

On TLC, the 2,2'-bipyrroles showed a strong fluorescence at 366 nm (UV-radiation). Photophysical properties are shown in Table 4. It was found that the 2,2'-bipyrroles are strongly luminescent materials at ambient temperature and the fluorescence quantum yields are between 0.45–0.72 in both non-polar solvent (DCM) and polar solvent (DMSO) systems. Meanwhile, large Stokes shifts were observed for these 2,2'-bipyrroles (varying between 63–84 nm). Thus, these 2,2'-bipyrroles might find applications in blue-light-emitting devices [18].

CONCLUSION

Based on a Pd(0) catalyzed coupling reaction, a series of 2,2'-bipyrroles were synthesized at ambient temperatures. Water plays important role in the reaction, and acetone/water was shown to be a very efficient system for the coupling of 2-iodopyrroles bearing a $\text{PhCH}_2\text{O}_2\text{C}$ substituent at the 5-position to generate the 2,2'-bipyrroles. These 2,2'-bipyrroles are highly luminescent materials with high fluorescence quantum yields and a large Stokes shift.

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Fig. 1.
Molecular structure of 2,2'-bipyrrole (**2c**). Only the major conformer is shown for each of the disordered phenyl groups

Table 1

2,2'-bipyrroles 2a–h from reductive coupling of 2-iodopyrroles under acetone/water conditions

Compound 1	R ¹	R ²	Compound 2	Yield, % ^a
1a	Me	Me	2a	4
1b	CH ₂ CH ₂ OMe	CO ₂ Me	2b	5
1c	Me	Me	2c	75
1d	Et	Me	2d	78
1e	Pr	Me	2e	49
1f	Me	CH ₂ CH ₂ CO ₂ Me	2f	51
1g	Me	Et	2g	7
1h	Me	CH ₂ CH ₂ CO ₂ Me	2h	12

^a Reaction conditions: 10% Pd-C/Zn, acetone/water, ambient temperature.

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Table 3

Reductive coupling of 2-iodopyrroles under toluene/water conditions

Compound 1	R ¹	R ²	Compound 2	Yield, % ^a
1a	Me	Me	2a	15
1b	CH ₂ CH ₂ OMe	CO ₂ Me	2b	45
1c	Me	Me	2c	76
1d	Et	Me	2d	77
1e	Pr	Me	2e	48
1f	Me	CH ₂ CH ₂ CO ₂ Me	2f	52
1g	Me	Et	2g	32
1h	Me	CH ₂ CH ₂ CO ₂ Me	2h	34

^a Reaction conditions: 10% Pd-C/Zn, toluene/water, ambient temperature.

Table 4

Photophysical data for the 2,2'-bipyroles in degassed dichloromethane (DCM) and dimethyl sulfoxide (DMSO) at ambient temperature

Compound	Solvent	$\lambda_{\text{max}}^{\text{abs}}$, nm(log <i>e</i>)	$\lambda_{\text{max}}^{\text{em}}$, nm ^a	Φ_{F} ^b	Stokes shift, nm
2a	DCM	229 (4.00), 317 (4.27)	382	0.55	65
	DMSO	315 (4.35)	379	0.65	64
2b	DCM	230 (4.47), 250 (4.56), 289 (4.32), 347 (4.48)	401	0.56	84
	DMSO	289 (4.31)	402	0.58	87
2c	DCM	229 (4.17), 319 (4.46)	386	0.52	67
	DMSO	318 (4.31)	381	0.72	63
2d	DCM	229 (4.11), 312 (4.26)	387	0.45	75
	DMSO	293 (4.44)	377	0.56	84
2e	DCM	209 (3.97), 319 (4.37)	387	0.56	68
	DMSO	317 (4.31)	381	0.67	64
2f	DCM	229 (3.85), 315 (3.95)	387	0.52	72
	DMSO	294 (4.12)	378	0.49	84
2g	DCM	229 (4.10), 318 (4.31)	384	0.50	68
	DMSO	313 (4.06)	381	0.71	68
2h	DCM	229 (4.02), 317 (4.22)	384	0.58	67
	DMSO	313 (4.38)	381	0.62	68

^a Excitation at 310 nm for all the compounds **2** in DCM and 290 nm for most of compounds **2** in DMSO except for **2a** and **2b** which were excited at 340 nm.

^b Quantum yields calculation for all the compounds **2** were based on quinine sulfate 5% H₂SO₄ solution ($\Phi_{\text{F}} = 0.56$) [14].