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The reaction of 1,4-naphthoquinone (**1**) with *N*-alkylpyrroles (**2**) gives a mixture of 2-(pyrrol-2-yl)-1,4-naphthoquinones (**3**) and 2,5-bis(1,4-naphthoquinon-2-yl)pyrroles (**4**). The yields and the ratios of these two products depend greatly on the experimental conditions. The reaction has been extended to 5-hydroxy-1,4-naphthoquinone (juglone, **5**) and 1,2-naphthoquinone (**6**). New pyrrolynaphthoquinones are obtained.

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Introduction.

Both pyrrole and quinone chemistry have been extensively studied [1,2] but very little is known about pyrrolynaphthoquinones [3-7]. We have previously reported the reaction of

indoles with 1,2- and 1,4-naphthoquinones [8] to prepare indolylquinones. We describe here our results on pyrrolynaphthoquinone chemistry and the synthesis of new organic dyes [9] by condensation of substituted pyrroles (**2a-h**) with 1,4-naphthoquinones (**1**), 5-hydroxy-1,4-naphthoquinone (juglone, **5**) and 1,2-naphthoquinone (**6**).

Results and Discussion.

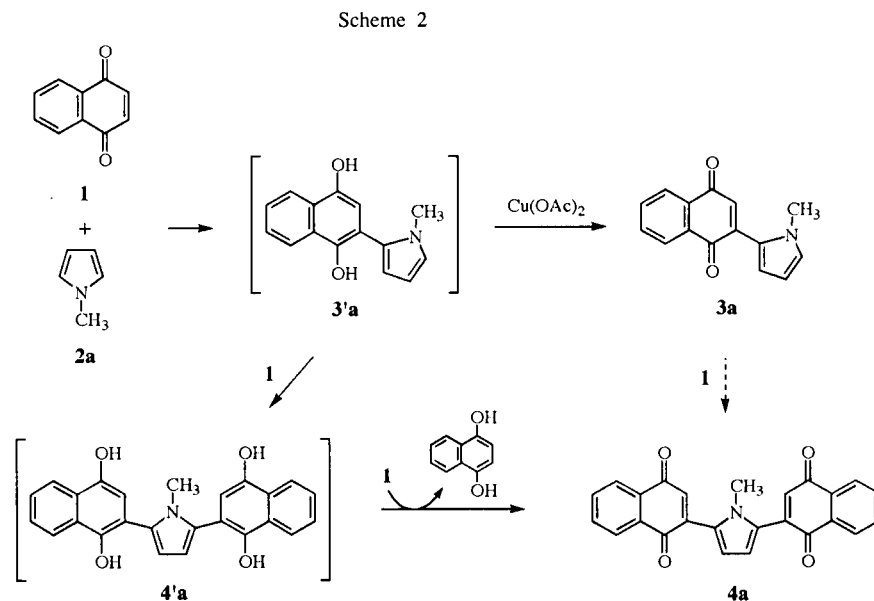
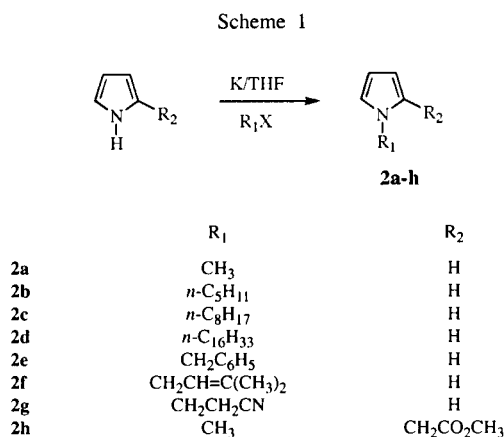
I- Synthesis of the *N*-Substituted Pyrroles (**2b-f**).

Pyrroles (**2a**, **2g**) and (**2h**) are commercially available. Pyrroles (**2b-f**) are obtained in good yields by alkylating the potassium salt of pyrrole with the corresponding alkyl halides [10].

II- Synthesis of Monopyrrolynaphthoquinones.

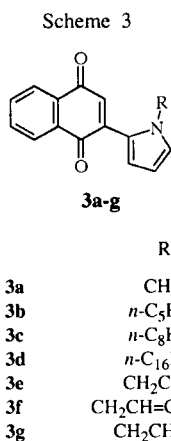
a) Condensation of Pyrroles (**2a-h**) with 1,4-Naphthoquinone.

The reaction of 1,4-naphthoquinone (**1**) with *N*-methylpyrrole (**2a**), the only reaction described in the literature [7], yields the mono- and diquinonylpyrroles after oxidation of



the intermediate naphthalenediols. Compound (**3a**) has been isolated in 79% yield using the experimental conditions [7]: excess of pyrrole (x 8), cupric acetate as the oxidising agent and acetic acid as the solvent at 25 °C (Table 1-method A).

Under the same conditions, pyrroles (**2b-g**) give poor yields of the monopyrrolylquinone (**3b-g**) (Table 1). Our work shows that this yield is increased by using chloroform with catalytic amounts of *p*-toluenesulfonic acid (Table 1-method B) and an excess of naphthoquinone or air to oxidise the intermediate hydroquinone (**3'**). This method avoids the use of metallic salts which are well known to polymerise pyrroles [11]. The optimal conditions are one mole of pyrrole for two moles of quinones in chloroform with a catalytic amount of *p*-toluenesulfonic acid at room temperature for five hours (Table 1-method C).



b) Condensation of Pyrroles with 5-Hydroxy-1,4-Naphthoquinone (Juglone).

The reaction of pyrroles with 5-hydroxy-1,4-naphthoquinone gives monopyrrolylated regioisomers juglones (**7**) and (**8**) in various proportions depending essentially on the pyrrole structure (Scheme 4).

c) Reaction of Pyrroles with 1,2-Naphthoquinone.

The expected compounds (**9a**) and (**9b**) are obtained in poor yields along with polymers and tars. In this case, the

method used has been previously described with indoles (Table 1-method D) [8h].

Scheme 5

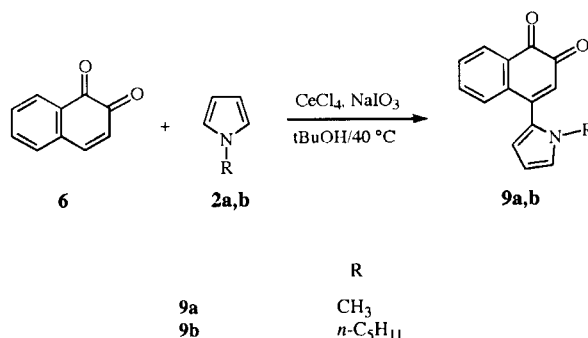
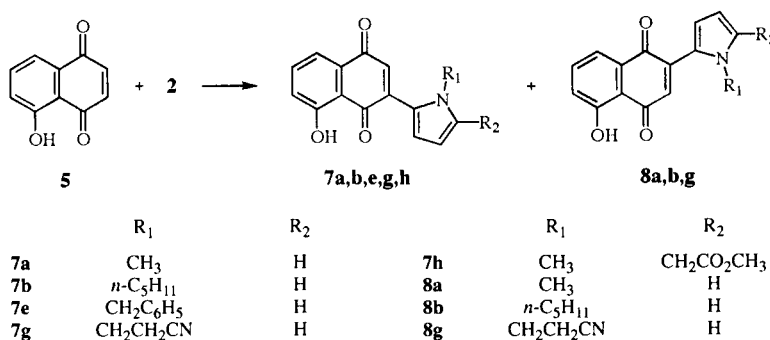


Table 1
Synthesis of (Pyrrol-2-yl)naphthoquinones
3a-e, **3g**, **7a**, **b**, **e**, **g**, **h**, **8a**, **b**, **g** and **9a,b**

Entry	Quinone	Pyrrole	Method	Compound	Yield (%)	M.p. (°C)
1	1	2a	A	3a	79	95-96
2		2b	A	3b	9	oil
3			B		15	
4			C		26	
5		2c	A	3c	11	oil
6			C		32	
7		2d	A	3d	28	56-57
8			C		41	
9		2e	A	3e	18	98-99
10			C		24	
11		2g	A	3g	26	127-128
12			C		42	
13	5	2a	A	7a-8a	90 (70/30) [a]	-
14		2b	A	7b-8b	51 (85/15)[a]	-
15		2e	A	7e	4	114-118
16			C		38	
17		2h	A	7h	10	129-131
18			C		76	
19		2g	A	7g-8g	0	-
20			C		17 (90/10) [a]	
21	6	2a	C	9a	6	125-126
22		2b	D	9b	17	oil

[a] Selectivity of the reaction.

Scheme 4



III- Synthesis of Bis-quinonylpyrroles (**4a-f**).

The described method using four moles of 1,4-naphthoquinone (**1**) and one mole of *N*-alkylpyrrole (**2**) in acetic acid at 50 °C for five hours furnishes compounds (**4b-f**) (Table II). It is only in the case of 1,4-naphthoquinone (**1**) that the bis-quinonylpyrrole structure (**4**) is obtained after oxidation of the intermediate hydroquinone (**4'**); neither with 5-hydroxy-1,4-naphthoquinone (juglone, **5**) nor with 1,2-naphthoquinone (**6**) are these compounds formed. The yield depends on the pyrrole structure (Table 2).

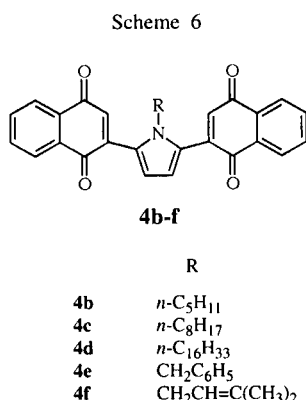


Table 2
Synthesis of 2,5-Bis(naphthoquinon-2-yl)pyrroles **4b-f**

Entry	Quinone	Pyrrole	Compound	Yield (%)	M.p. (°C)
23	1	2b	4b	87	127-128
24		2c	4c	49	75-76
25		2d	4d	38	40-43
26		2e	4e	10	156-157
27		2f	4f	9	149-150

In this work we have prepared new pyrrolylquinones from 1,4-naphthoquinone (**1**), 5-hydroxy-1,4-naphthoquinone (**5**) and 1,2-naphthoquinone (**6**). The yields of the reaction depend essentially on the experimental conditions and the structure of the pyrrole. Only with 1,4-naphthoquinone (**1**) are the bis-quinonyls obtained.

EXPERIMENTAL

With the exception of compounds **1**, **2a**, **2g**, **2h**, **5** and **6** purchased from Aldrich, all other products were prepared. Melting points were taken on a Mettler FP 5 capillary melting-point apparatus and are uncorrected. The ir spectra were recorded on a Perkin-Elmer 781 Spectrophotometer. The uv spectra were performed on a Shimadzu UV/Vis 240 Spectrophotometer. The ¹H and ¹³C nmr spectra were run on a Bruker W 200 Spectrophotometer at 200 MHz and 50 MHz respectively, using CDCl₃ as the solvent and tetramethylsilane (TMS) as the internal standard. The mass spectra were scanned on a Finnigan Mat 800 ITD coupled with a CP - Sil 5 GC column (chemical ionisation using isobutane) or a Nermag R-30-10 (with direct introduction, chemical

ionisation using NH₃). Tlc was performed on Silica gel 60 F₂₅₄ (Merck, Darmstadt), and column chromatographs on Matrex LC 60A (silica gel, 35-70 μm, Grace Davidson, Molsheim). The High Resolution Mass Spectra (HRMS) were obtained at the Laboratoire de l'Activation Moléculaire of the Ecole Normale Supérieure; HRMS was used instead of microanalysis due to the instability of the compounds produced. Organic solutions, after drying with anhydrous MgSO₄, were concentrated at T° < 60 °C under reduced pressure.

Synthesis of *N*-alkylpyrroles.

N-Pentylpyrrole (**2b**).

Small pieces of freshly cut potassium metal (8.1 g, 207 mmol) were added to a solution of 20 mL (287 mmol) of pyrrole in 200 mL of tetrahydrofuran (THF) with stirring. The reaction was conducted under dry argon. The mixture was stirred for 2 hours and then was warmed until all traces of potassium had disappeared. When the potassium was completely consumed, the reaction mixture was allowed to cool to room temperature. A solution of 24.8 mL (0.2 mol) of *n*-pentyl bromide in 50 mL of THF was added dropwise over a period of 1 hour. The reaction mixture was stirred for an additional 12 hours and then diluted with 100 mL of water and extracted twice with diethyl ether (2 X 50 mL). The combined organic phases were washed with water (100 mL) and dried over MgSO₄. Ether was removed *in vacuo* and distillation of the oily residue afforded (**2b**, 23.3 g, 170 mmol, 85%); bp 78-82 °C (15 Torr), 42-43 °C (0.5 Torr) [12]; ms (isobutane) *m/z* 138 (MH⁺); ¹H nmr (CDCl₃) δ 1.00 (t, 3H, J = 6.0 Hz), 1.28-1.55 (m, 4H), 1.86 (quint, 2H, J = 7.3 Hz), 3.95 (t, 2H, J = 7.3 Hz), 6.24 (m, 2H), 6.74 (m, 2H).

N-Octylpyrrole (**2c**).

Compound **2c** was prepared, analogously to the preparation of **2b**, from potassium metal (8.1 g, 207 mmol), pyrrole (20 mL, 287 mmol) and *n*-octyl bromide (38.6 g, 0.2 mol). Distillation under reduced pressure gave (**2c**, 27.9 g, 0.156 mol, 78%); bp 127-130 °C (13 Torr); ms (isobutane) *m/z* 180 (MH⁺); ¹H nmr (CDCl₃) δ 0.98 (t, 3H, J = 6.6 Hz), 1.2-1.5 (m, 10H), 1.84 (quint, 2H, J = 6.8 Hz), 3.94 (t, 2H, J = 6.8 Hz), 6.22 (m, 2H), 6.73 (m, 2H).

N-Hexadecylpyrrole (**2d**).

Compound **2d** was prepared, analogously to the preparation of **2b**, from potassium metal (8.1 g, 207 mmol), pyrrole (20 mL, 287 mmol) and *n*-hexadecyl bromide (61.1 g, 0.2 mol). Distillation under reduced pressure gave (**2d**, 46.6 g, 0.160 mol, 80%); bp 146-147 °C (3 x 10⁻² Torr); ms (isobutane) *m/z* 292 (MH⁺); ¹H nmr (CDCl₃) δ 0.89 (t, 3H, J = 6.8 Hz), 1.12-1.38 (m, 26H), 1.77 (quint, 2H, J = 7.0 Hz), 3.87 (t, 3H, J = 7.0 Hz), 6.15 (m, 2H), 6.60 (m, 2H).

N-Benzylpyrrole (**2e**).

Compound **2e** was prepared, analogously to the preparation of **2b**, from potassium metal (8.1 g, 207 mmol), pyrrole (20 mL, 287 mmol) and benzyl bromide (34.2 g, 0.2 mol). Distillation under reduced pressure gave **2e** (20.1 g, 0.128 mol, 64%); bp 90-94 °C (1 Torr), 88-90 (0.8-0.9 Torr) [13]; ms (isobutane) *m/z* 158 (MH⁺); ¹H nmr (CDCl₃) δ 5.12 (s, 2H), 6.26 (m, 2H), 6.76 (m, 2H), 7.14-7.19 (m, 2H), 7.29-7.39 (m, 3H).

N-(3-Methyl-but-2-en-1-yl)pyrrole (**2f**).

Compound (**2f**) was prepared, analogously to the preparation of (**2b**), from potassium metal (8.1 g, 207 mmol), pyrrole (20 mL,

287 mmol) and 1-chloro-3-methyl-but-2-ene (22.5 mL, 0.2 mol). Distillation under reduced pressure gave (**2f**, 22.95 g, 0.17 mol, 85%); bp 90–92 °C (15 Torr); ms (isobutane) *m/z* 136 (MH⁺); ¹H nmr (CDCl₃) δ 1.84 (s, 6H), 4.54 (d, 2H, *J* = 7.2 Hz), 5.48 (t, 1H, *J* = 7.2 Hz), 6.24 (m, 2H), 6.74 (m, 2H).

Synthesis of 2-(Pyrrol-2-yl)-1,4-naphthoquinones.

Method A [8].

2-(1-Methyl-1*H*-pyrrol-2-yl)-1,4-naphthoquinone (**3a**).

To a solution of 1,4-naphthoquinone (**1**, 1.15 g, 9.48 mmol) in glacial acetic acid (50 mL) was added copper acetate monohydrate (1.88 g, 9.48 mmol) and *N*-methylpyrrole (**2a**, 7.3 mL, 76 mmol), and the mixture was stirred for 1 hour at room temperature. The solvent was removed *in vacuo* and the residue was dissolved in chloroform (50 mL) and water (50 mL). The aqueous phase was washed with a saturated solution of sodium carbonate, and then the organic phase was collected. The aqueous phase was extracted again with chloroform (50 mL) and the combined organic solutions were washed with water (50 mL), dried (MgSO₄) and concentrated *in vacuo*. Purification of the residue by column chromatography [SiO₂, CHCl₃] afforded the title compound **3a** as a red solid (1.77 g, 7.49 mmol, 79%); mp 95–96 °C; ms (isobutane) *m/z* 238 (MH⁺); ¹H nmr (CDCl₃) δ 3.70 (s, 3H), 6.28 (dd, 1H, *J* = 2.6 Hz, 3.9 Hz), 6.68 (dd, 1H, *J* = 1.7 Hz, 3.9 Hz), 6.88–6.91 (m, 2H), 7.73–7.80 (m, 2H), 8.08–8.18 (m, 2H); uv (THF) λ_{max} (lg ε) = 248 (3.90), 292 (3.95), 481 (3.68); ir (KBr) ν 1650, 1665 cm^{−1} (C=O).

Method B.

2-(1-Pentyl-1*H*-pyrrol-2-yl)-1,4-naphthoquinone (**3b**).

To a solution of compound (**1**, 1 g, 6.32 mmol) in chloroform (50 mL) *N*-pentylpyrrole (**2b**, 6.9 g, 50.5 mmol) was added and then stirred with a trace of *p*-toluenesulfonic acid for 1 hour at room temperature. The mixture was diluted with chloroform (100 mL) and washed with water (4 × 100 mL) and then with a brine solution (50 mL). The organic solution was dried (MgSO₄) and concentrated *in vacuo*. The residue was chromatographed on silica gel [SiO₂, CHCl₃] to give (**3b**, 278 mg, 0.95 mmol, 15%) as a red oil; ms (isobutane) *m/z* 294 (MH⁺); ¹H nmr (CDCl₃) δ 0.84 (t, 3H, *J* = 6.8 Hz), 1.16–1.34 (m, 4H), 1.73 (quint, 2H, *J* = 7.2 Hz), 3.94 (t, 2H, *J* = 7.6 Hz), 6.29 (dd, 1H, *J* = 2.7 Hz, 3.7 Hz), 6.59 (dd, 1H, *J* = 1.7 Hz, 3.7 Hz), 6.88 (s, 1H), 6.97 (m, 1H), 7.72–7.81 (m, 2H), 8.10–8.19 (m, 2H); uv (THF) λ_{max} (lg ε) = 245 (4.20), 288 (4.01), 482 (3.68); ir (CH₂Cl₂) ν 1655, 1675 cm^{−1} (C=O); hrms (CI) *m/z* Calcd. for C₁₉H₂₀NO₂ (MH⁺): 294.1494; Found: 294.1495.

2-(1-Octyl-1*H*-pyrrol-2-yl)-1,4-naphthoquinone (**3c**).

Compound **3c** was prepared, analogously to the preparation of **3a**, from *N*-octylpyrrole (**2c**, 4 g, 22.35 mmol), copper acetate monohydrate (555 mg, 2.79 mmol) and (**1**, 441 mg, 2.79 mmol). Column chromatography [SiO₂, CHCl₃] gave (**3c**, 104 mg, 0.31 mmol, 11%) as a red oil; ms (isobutane) *m/z* 336 (MH⁺); ¹H nmr (CDCl₃) δ 0.84 (t, 3H, *J* = 6.8 Hz), 1.1–1.4 (m, 10H), 1.71 (quint, 2H, *J* = 7.4 Hz), 3.94 (t, 2H, *J* = 7.4 Hz), 6.29 (dd, 1H, *J* = 2.7 Hz, 3.8 Hz), 6.59 (dd, 1H, *J* = 1.7 Hz, 3.8 Hz), 6.88 (s, 1H), 6.97 (dd, 1H, *J* = 1.7, 2.7 Hz), 7.72–7.81 (m, 2H), 8.10–8.19 (m, 2H); uv (THF) λ_{max} (lg ε) = 246 (4.17), 288 (3.99), 483 (3.67); ir (CH₂Cl₂) 1655, 1675 cm^{−1} (C=O); hrms (CI) *m/z* Calcd. for C₂₂H₂₆NO₂ (MH⁺): 336.1964; Found: 336.1957.

2-(1-Hexadecyl-1*H*-pyrrol-2-yl)-1,4-naphthoquinone (**3d**).

Compound **3d** was prepared, analogously to the preparation of **3a**, from *N*-hexadecylpyrrole (**2d**, 3.68 g, 12.64 mmol), copper acetate monohydrate (310 mg, 1.58 mmol) and (**1**, 250 mg, 1.58 mmol). Column chromatography [SiO₂, CHCl₃] gave (**3d**, 198 mg, 0.44 mmol, 28%) as a red solid; mp 56–57 °C; ms (isobutane) *m/z* 448 (MH⁺); ¹H nmr (CDCl₃) δ 0.88 (t, 3H, *J* = 6.8 Hz), 1.1–1.4 (m, 26H), 1.58 (quint, 2H, *J* = 7.5 Hz), 3.94 (t, 2H, *J* = 7.5 Hz), 6.29 (dd, 1H, *J* = 2.7 Hz, 3.8 Hz), 6.59 (dd, 1H, *J* = 1.7 Hz, 3.8 Hz), 6.88 (s, 1H), 6.96 (m, 1H), 7.75–7.79 (m, 2H), 8.10–8.19 (m, 2H); uv (THF) λ_{max} (lg ε) = 247 (4.19), 485 (3.62); ir (KBr) ν 1640, 1675 cm^{−1} (C=O); hrms (CI) *m/z* Calcd. for C₃₀H₄₂NO₂ (MH⁺): 448.3216; Found: 448.3221.

Method C.

2-(1-Benzyl-1*H*-pyrrol-2-yl)-1,4-naphthoquinone (**3e**).

Method C proceeds as Method B except for the differences in the mole ratios of the reactants. To a solution of compound (**1**, 1 g, 6.33 mmol) in chloroform (50 mL) *N*-benzylpyrrole (**2e**, 496 mg, 3.16 mmol) was added and the solution was stirred with a trace of *p*-toluenesulfonic acid for 5 hours at room temperature. The reaction mixture was treated as that of Method B. Purification of the residue by column chromatography [SiO₂, CHCl₃] afforded the red solid (**3e**, 237 mg, 0.76 mmol, 24%); mp 98–99 °C; ms (isobutane) *m/z* 314 (MH⁺); ¹H nmr (CDCl₃) δ 5.19 (s, 2H), 6.34 (dd, 1H, *J* = 2.8 Hz, 3.8 Hz), 6.66 (dd, 1H, *J* = 1.7 Hz, 3.8 Hz), 6.78 (s, 1H), 6.94–7.02 (m, 3H), 7.18–7.29 (m, 3H), 7.69–7.78 (m, 2H), 8.00–8.07 (m, 1H), 8.11–8.19 (m, 1H); uv (THF) λ_{max} (lg ε) = 246 (4.19), 290 (4.01), 477.5 (3.66); ir (KBr) ν 1640, 1670 cm^{−1} (C=O); hrms (CI) *m/z* Calcd. for C₂₁H₁₆NO₂ (MH⁺): 314.1181; Found: 314.1184.

3-[2-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)-pyrrol-1-yl]propionitrile (**3g**).

Compound **3g** was prepared, analogously to the preparation of **3e**, from 3-(pyrrol-1-yl)propionitrile (379 mg, 3.16 mmol) and (**1**, 1 g, 6.33 mmol). Column chromatography [SiO₂, CHCl₃] gave (**3g**, 237 mg, 1.33 mmol) as a red solid in 42% yield; mp 127–128 °C; ms (isobutane) *m/z* 277 (MH⁺); ¹H nmr (CDCl₃) δ 2.89 (t, 2H, *J* = 6.8 Hz), 4.18 (t, 2H, *J* = 6.8 Hz), 6.34 (dd, 1H, *J* = 3.7 Hz, 2.8 Hz), 6.51 (dd, 1H, *J* = 3.7 Hz, 1.7 Hz), 6.98 (s, 1H), 7.06 (dd, 1H, *J* = 2.8 Hz, 1.7 Hz), 7.77–7.83 (m, 2H), 8.10–8.18 (m, 2H); uv (THF) λ_{max} (lg ε) = 247 (4.08), 266 (4.00), 292 (3.85), 335 (3.57), 469 (3.60); ir (KBr) ν 1650, 1675 cm^{−1} (C=O); hrms (CI) *m/z* Calcd. for C₁₇H₁₃N₂O₂ (MH⁺): 277.0977; Found: 277.0973.

3-(1-Methyl-1*H*-pyrrol-2-yl)-5-hydroxy-1,4-naphthoquinone (**7a**) and 2-(1-methyl-1*H*-pyrrol-2-yl)-5-hydroxy-1,4-naphthoquinone (**8a**).

To a solution of juglone (**5**, 1 g, 5.75 mmol) and copper acetate monohydrate (1.15 g, 5.75 mmol) in glacial acetic acid was added *N*-methylpyrrole (**2a**, 3.74 g, 46.24 mmol) and the mixture was stirred for 4 hours at room temperature. After the usual reaction work up (see compound **3a**), the product was chromatographed on silica gel [SiO₂, CHCl₃] to give a mixture of (**7a** and **8a**, 1.31 g, 5.18 mmol, 90%). A sample of the mixture was purified by preparative layer chromatography on silica gel to give (**7a** and **8a**) as pure compounds.

Compound **7a**; mp 119–120 °C; ms (isobutane) *m/z* 254 (MH⁺); ¹H nmr (CDCl₃) δ 3.72 (s, 3H), 6.29 (dd, 1H, *J* = 2.6 Hz,

3.8 Hz), 6.68 (dd, 1H, $J = 1.8$ Hz, 3.8 Hz), 6.81 (s, 1H), 6.92 (m, 1H), 7.22-7.31 (m, 1H), 7.60-7.68 (m, 2H), 12.19 (s, 1H); ^{13}C nmr (CDCl_3) δ 36.2, 109.5, 115.3, 117.2, 118.4, 124.2, 125.7, 129.2, 132.1, 132.6, 136.5, 139.4, 161.7, 183.8, 189.8; uv (THF) λ_{max} (lg ϵ) = 247 (4.26), 285 (4.14), 427 (3.93), 470 (3.88); ir (KBr) ν 1635, 1670 cm^{-1} (C=O); hrms (CI) m/z Calcd. for $\text{C}_{15}\text{H}_{12}\text{NO}_3$ (MH^+): 254.0817; Found: 254.0810.

Compound **8a**; mp 125-126 °C; ms (isobutane) m/z 254 (MH^+); ^1H nmr (CDCl_3) δ 3.72 (s, 3H), 6.29 (dd, 1H, $J = 2.6$ Hz, 3.8 Hz), 6.74 (dd, 1H, $J = 1.8$ Hz, 3.8 Hz), 6.83 (s, 1H), 6.93 (m, 1H), 7.26-7.30 (m, 1H), 7.59-7.70 (m, 2H), 12.18 (s, 1H); ^{13}C nmr (CDCl_3) δ 36.4, 109.7, 115.0, 118.0, 119.6, 124.1, 126.6, 129.9, 130.8, 132.4, 135.9, 140.5, 160.9, 183.7, 189.8; ir (KBr) ν 1635, 1670 cm^{-1} (C=O); hrms (CI) m/z Calcd. for $\text{C}_{15}\text{H}_{12}\text{NO}_3$ (MH^+): 254.0817; Found: 254.0814.

3-(1-Benzyl-1H-pyrrol-2-yl)-5-hydroxy-1,4-naphthoquinone (**7e**).

Compound **7e** was prepared, analogously to the preparation of **3e**, from *N*-benzylpyrrole (**2e**, 677 mg, 4.31 mmol) and (**5**, 1.5 g, 8.62 mmol). Column chromatography [SiO_2 , CHCl_3] gave (**7e**, 550 mg, 1.66 mmol, 39%) as a red solid; mp 114-115 °C; ms (70 eV) m/z 329 (M^+ , 20), 284 (7), 252 (5), 91 (100); ^1H nmr (CDCl_3) δ 5.24 (s, 2H), 6.39 (m, 1H), 6.70 (m, 1H), 6.75 (s, 1H), 7.01 (m, 3H), 7.30 (m, 4H), 7.64-7.68 (m, 2H), 12.20 (s, 1H); uv (THF) λ_{max} (lg ϵ) = 243 (4.21), 284 (4.06), 427 (3.87); ir (KBr) ν 1635, 1650 cm^{-1} (C=O); hrms (CI) m/z Calcd. for $\text{C}_{21}\text{H}_{16}\text{NO}_3$ (MH^+): 330.1130; Found: 330.1123.

Methyl [5-(5-hydroxy-1,4-dioxo-1,4-dihydronaphthalen-3-yl)-1-methyl-1H-pyrrol-2-yl] acetate (**7h**).

Compound **7h** was prepared, analogously to the preparation of **3e**, from methyl (1-methyl-1H-pyrrol-2-yl)acetate (220 mg, 1.44 mmol) and (**5**, 500 mg, 2.87 mmol). Column chromatography [SiO_2 , CHCl_3] gave (**7h**, 378 mg, 1.16 mmol, 76%) as red crystals; mp 129-131 °C; ms (NH_3) m/z 343 (MNH_4^+ , 100), 326 (MH^+ , 78), 266 (M-COOCH_3 , 15); ^1H nmr (CDCl_3) δ 3.59 (s, 3H), 3.75 (s, 2H), 3.76 (s, 3H), 6.23 (d, 1H, $J = 3.8$ Hz), 6.60 (d, 1H, $J = 3.8$ Hz), 6.84 (s, 1H), 7.29-7.31 (m, 1H), 7.64-7.67 (m, 2H), 12.19 (s, 1H); uv (THF) λ_{max} (lg ϵ) = 258 (4.18), 290 (3.99), 428 (3.61), 514 (3.61); ir (KBr) ν 1635, 1650 cm^{-1} (C=O), 1745 cm^{-1} (C=O, ester); hrms (CI) m/z Calcd. for $\text{C}_{18}\text{H}_{16}\text{NO}_5$ (MH^+): 326.1028; Found: 326.1031.

Synthesis of 2,5-Bis(naphthoquinon-2-yl)pyrroles.

1-Pentyl-2,5-bis(1,4-naphthoquinon-2-yl)pyrrole (**4b**).

To a solution of 1,4-naphthoquinone (**1**, 9.23 g, 58.4 mmol) in acetic acid (50 mL) was added *N*-pentylpyrrole (**2b**, 2 g, 14.6 mmol) and the mixture stirred for 5 hours at 50 °C. The solvent was removed *in vacuo* and the residue was added to a 1:1 mixture (100 mL) of chloroform and water. To the mixture was added a saturated solution of sodium carbonate (20 mL), and then the organic phase was collected. The aqueous phase was extracted with chloroform (50 mL) and the combined organic solutions were washed with water (50 mL), dried (MgSO_4) and concentrated *in vacuo*. Purification of the residue by column chromatography [SiO_2 , CHCl_3] afforded the title compound **4b** as a red solid (5.8 g, 12.92 mmol, 87%); mp 127-128 °C; ms (NH_3) m/z 467 (MNH_4^+ , 8), 450 (MH^+ , 34); ^1H nmr (CDCl_3) δ 0.65 (t, 3H, $J = 7.2$ Hz), 0.78-1.06 (m, 4H), 1.36 (quint, 2H, $J = 7.4$ Hz), 4.00 (t, 2H, $J = 7.4$ Hz), 6.62 (s, 2H), 7.04 (s, 2H), 7.73-7.83 (m, 4H),

8.05-8.23 (m, 4H); uv (THF) λ_{max} (lg ϵ) = 246 (4.49), 514 (3.90); ir (KBr) ν 1650, 1670 cm^{-1} (C=O).

1-Octyl-2,5-bis(1,4-naphthoquinon-2-yl)pyrrole (**4c**).

Compound **4c** was prepared, analogously to the preparation of **4b**, from *N*-octylpyrrole (**2c**, 2 g, 11.2 mmol) and (**1**, 7.1 g, 44.7 mmol). Column chromatography [SiO_2 , CHCl_3] gave (**4c**, 2.7 g, 5.5 mmol, 49%) as a red solid; mp 75-76 °C; ms (NH_3) m/z 509 (MNH_4^+ , 100), 492 (MH^+ , 15); ^1H nmr (CDCl_3) δ 0.73 (t, 3H, $J = 7.0$ Hz), 0.88-1.12 (m, 10H), 1.39 (quint, 2H, $J = 7.2$ Hz), 4.00 (t, 2H, $J = 7.2$ Hz), 6.62 (s, 2H), 7.05 (s, 2H), 7.74-7.83 (m, 4H), 8.04-8.22 (m, 4H); uv (THF) λ_{max} (lg ϵ) = 242 (4.37), 288 (3.93), 512 (3.62); ir (KBr) ν 1650, 1670 cm^{-1} (C=O); hrms (CI) m/z Calcd. for $\text{C}_{32}\text{H}_{30}\text{NO}_4$ (MH^+): 492.2175; Found: 492.2183.

1-Hexadecyl-2,5-bis(1,4-naphthoquinon-2-yl)pyrrole (**4d**).

Compound **4d** was prepared, analogously to the preparation of **4b**, from *N*-hexadecylpyrrole (**2d**, 4 g, 13.75 mmol) and (**1**, 8.7 g, 55.0 mmol). Column chromatography [SiO_2 , CHCl_3] gave (**4d**, 3.15 g, 5.23 mmol, 38%) as a red solid; mp 40-43 °C; ms (NH_3) m/z 622 (MNH_4^+ , 100), 605 (MH^+ , 15); ^1H nmr (CDCl_3) δ 0.88 (t, 3H, $J = 6.7$ Hz), 0.99-1.41 (m, 28H), 4.00 (t, 2H, $J = 7.3$ Hz), 6.62 (s, 2H), 7.04 (s, 2H), 7.75-7.85 (m, 4H), 8.06-8.23 (m, 4H); uv (THF) λ_{max} (lg ϵ) = 246 (4.66), 511 (3.83). ir (KBr) ν 1660 cm^{-1} (C=O); hrms (CI) m/z Calcd. for $\text{C}_{40}\text{H}_{46}\text{NO}_4$ (MH^+): 604.3427; Found: 604.3422.

1-Benzyl-2,5-bis(1,4-naphthoquinon-2-yl)pyrrole (**4e**).

Compound **4e** was prepared, analogously to the preparation of **4b**, from *N*-benzylpyrrole (**2e**, 4 g, 25.5 mmol) and (**1**, 16.1 g, 102.0 mmol). Column chromatography [SiO_2 , CHCl_3] gave (**4e**, 1.12 g, 2.39 mmol, 10%) as a red solid; mp 156-157 °C; ms (NH_3) m/z 487 (MNH_4^+ , 95), 470 (MH^+ , 100); ^1H nmr (CDCl_3) δ 5.20 (s, 2H), 6.64-6.67 (m, 4H), 6.85 (s, 2H), 6.94-7.00 (m, 3H), 7.75-7.82 (m, 4H), 8.03-8.08 (m, 2H), 8.16-8.20 (m, 2H); uv (THF) λ_{max} (lg ϵ) = 245 (4.43), 285 (4.33), 512 (4.02). ir (KBr) ν 1650, 1670 cm^{-1} (C=O); hrms (CI) m/z Calcd. for $\text{C}_{31}\text{H}_{20}\text{NO}_4$ (MH^+): 470.1392; Found: 470.1386.

1-(3-Methyl-2-buten-1-yl)-2,5-bis(1,4-naphthoquinon-2-yl)pyrrole (**4f**).

Compound **4f** was prepared, analogously to the preparation of **4b**, from 1-(3-methyl-but-2-en-1-yl)pyrrole (**2f**, 3 g, 22.2 mmol) and (**1**, 14.05 g, 88.9 mmol). Column chromatography [SiO_2 , CHCl_3] gave (**4f**, 0.89 g, 1.99 mmol, 9%) as a red solid; mp 149-150 °C; ms (NH_3) m/z 465 (MNH_4^+ , 100), 448 (MH^+ , 78); ^1H nmr (CDCl_3) δ 1.24 (d, 3H, $J = 1.1$ Hz), 1.38 (s, 3H), 4.58 (d, 2H, $J = 6.2$ Hz), 4.95 (t, 1H), 6.63 (s, 2H), 6.99 (s, 2H), 7.75-7.84 (m, 4H), 8.11-8.20 (m, 4H); uv (THF) λ_{max} (lg ϵ) = 246.5 (4.39), 292 (4.19), 507 (3.91); ir (KBr) ν 1650, 1670 cm^{-1} (C=O), 1655 cm^{-1} (C=C); hrms (CI) m/z Calcd. for $\text{C}_{29}\text{H}_{22}\text{NO}_4$ (MH^+): 448.1549; Found: 448.1552.

Synthesis of 4-(1-Pyrrol-2-yl)-1,2-naphthoquinones

4-(1-Methylpyrrol-2-yl)-1,2-naphthoquinone (**9a**).

Compound **9a** was prepared, analogously to the preparation of **3e**, from 1-methylpyrrole (**2a**, 1 g, 12.35 mmol) and (**6**, 1.95 g, 12.35 mmol). Column chromatography [SiO_2 , $\text{CHCl}_3/\text{MeOH}$ (99:1)] gave (**9a**, 172 mg, 0.72 mmol, 6%) as a red solid; mp 125-126 °C; ms (isobutane) m/z 238 (MH^+ , 100), 209 (16), 181 (4); ^1H nmr (CDCl_3) δ 3.67 (s, 3H), 6.35 (m, 2H), 6.50 (dd, 1H, $J =$

3.8 Hz, 1.6 Hz), 6.92 (m, 1H), 7.52-7.64 (m, 3H), 8.19-8.22 (m, 1H); uv (THF) λ_{max} (lg ϵ) = 241 (4.03), 290 (3.78), 455 (3.13); ir (KBr) ν 1645 cm^{-1} (C=O).

Method D.

4-(1-Pentylpyrrol-2-yl)-1,2-naphthoquinone (**9b**).

To a solution of 1,2-naphthoquinone (**6**, 1 g, 6.33 mmol) and cerium chloride heptahydrate (2.35 g, 6.33 mmol) in 250 mL of *tert*-butanol at 40 °C was added sodium iodate (1.25 g, 6.33 mmol) and then *N*-pentylpyrrole (**2b**, 0.87 g, 6.33 mmol). The reaction mixture was stirred for 30 minutes at room temperature and the solvent was evaporated. The crude mixture was dissolved in chloroform (50 mL), washed with water, and the organic solution dried over MgSO_4 . Removal of the solvent under reduced pressure afforded a residue which was chromatographed on silica gel [SiO_2 , $\text{CHCl}_3/\text{MeOH}$ (99:1)] to give (**9b**, 319 mg, 1.09 mmol, 17%) as a red oil; ms (isobutane) m/z 294 (MH^+ , 100), 265 (10); ^1H nmr (CDCl_3) δ 0.78 (t, 3H), 1.0-1.3 (m, 4H), 1.65 (quint, 2H, $J = 7.2$ Hz), 3.92 (t, 2H, $J = 7.2$ Hz), 6.33 (dd, 1H, $J = 3.8$ Hz, 2.8 Hz), 6.38 (s, 1H), 6.44 (dd, 1H, $J = 3.8$ Hz, 1.6 Hz), 6.98 (m, 1H), 7.50-7.68 (m, 3H), 8.18-8.23 (m, 1H); uv (THF) λ_{max} (lg ϵ) = 246 (4.45), 288 (3.85), 322 (3.84), 469 (3.56); ir (KBr) ν 1645 cm^{-1} (C=O).

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