Substituted 1,10-Phenanthroline-5,6-diamines and their Extension to Soluble, Acetylenic Pyrazinophenanthrolines

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Received 16 February 2005; revised 1 June 2005

Abstract: 2,9-Disubstituted and 3,8-disubstituted 1,10-phenanthrolines have been converted to the respective 5,6-diamines in three steps. The new heterocycles have been employed in condensation reactions with a protected 1,2-dialkynyl-1,2-dione to afford solubility-improved, acetylenic pyrazinophenanthrolines (pyzphen). In an initial study, the synthetic scope of these novel acetylenic ligands is evaluated.

Key words: acetylenes, condensation, ligands, solubility, synthesis

Aromatic N-heterocycles of the 1,10-phenanthroline type (phen) have been used extensively as chelating agents for transition metals, in particular for the bis(bipyridyl)ruthenium(II) fragment.[3] Extended N-heterocyclic aromatic ligands such as pyrazinophenanthrolines (pyzphen) or dipyridophenazines (dppz) feature lower π* orbitals and, hence, are better electron acceptors than the phen moiety itself (Figure 1).[4]

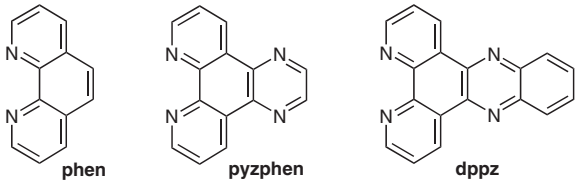


Figure 1

In ruthenium(II) complexes of pyzphen and dppz, the light-induced charge-separated state is directed towards these ligands. The complexes have thus found applications as luminescent probes of many aprotic microenvironments, including those of polymer films, micelles and of DNA.[3–5] More recently, dinuclear complexes of ruthenium with extended N-heterocyclic bridging ligands were demonstrated to be multi-electron acceptors and up to four electrons could be accumulated in a system having two dppz units fused back-to-back.[6] The ability to store four electrons is a vital aspect for the oxidation of water in natural and artificial photosynthesis.[7] Despite these appealing prospects, the variety of bridging ligands where the phen coordination sites are fused by a number of benzannulated rings is limited, a fact that is caused in great part by the compounds' low solubilities. Due to aggregation phenomena, chemical transformations on extended planar π-systems are generally difficult to be carried out.[8]

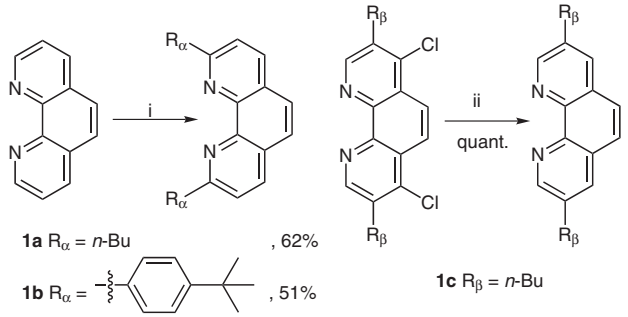
Complexations to metal fragments have frequently been used to increase the solubility of the otherwise sparingly soluble ligands.[8] However, this strategy constitutes not only a limitation to the design, but also prevents an evaluation of the (photo)physical properties of the chelating heterocycle itself. An alternative approach has been the introduction of bulky solubilizing substituents to prevent the heterocycles from π-stacking. This very successful strategy has been employed to increase the solubility of monomeric[9,10] as well as oligomeric phen derivatives.[11] However, solubility limitations are an even greater issue in systems with a higher degree of aromatic ring annulation such as pyzphen or dppz. We thus decided to adopt the strategy which has been found viable for the solubilization of phen and to exploit it for the preparation of soluble pyzphen heterocycles. In our earlier work we have experienced that a terminally unprotected, diacetylenic pyzphen is literally insoluble in any organic solvent.[12] This compound is thus a good reference to study the solubilizing properties of newly introduced substituents and we embarked on the synthesis of acetylenic pyzphen heterocycles bearing bulky alkyl or aryl substituents. Soluble acetylenic pyzphen may open new pathways for further functionalization of the acetylene or the construction of highly unsaturated carbon scaffolds with annulated metal binding sites.[13]

As pyzphens can be derived from the condensation of phen-5,6-diamines with suitable 1,2-diketones, it seemed desirable to have the substituents on equivalent positions around the phen core to avoid complex spectroscopic data. Introduction of substituents in the α positions of phen can be achieved in a Ziegler reaction.[14]

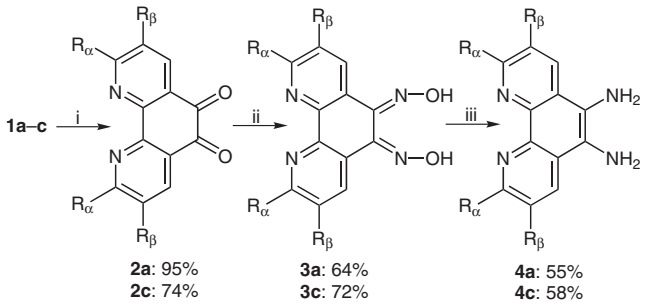
Following the general protocol, butyl lithium and 4-*tert*-butylphenyl lithium[15] were reacted separately with dry phen, resulting in the addition of the organolithium reagent to both pyridine subunits of phen. Subsequent hydrolysis and dehydrogenation of the intermediate with manganese(IV) oxide affords the 2,9-disubstituted phen analogues in 62% and 51% yield, respectively (Scheme 1).

Substitution of phen in the β positions was found to be more difficult and required a multi-step sequence. Only a few examples in the literature address the synthesis of these compounds,[10] one of which describes the synthesis of 3,8-dibutyl-4,7-dichloro-phen in four steps on a gram-

SYNTHESIS 2005, No. 18, pp 3135–3139
Advanced online publication: 26.08.2005
DOI: 10.1055/s-2005-916010; Art ID: T01905SS



Scheme 1 *Reagents and conditions:* (i) 1) R_α-Li, toluene, 16 h, r.t.; 2) H_2O; 3) MnO_2, 62% for **1a**, 51% for **1b**. (ii) Zinc, AcOH, Δ, 3 d, quant.



Scheme 2 *Reagents and conditions:* (i) KBr, concd HNO_3, concd H_2SO_4, Δ, 2 h, 95% for **2a**, 74% for **2c**. (ii) $NH_2OH{\cdot}HCl$, $BaCO_3$, EtOH, Δ, 16 h, 64% for **3a**, 72% for **3c**. (iii) hydrazine, Pd/C, EtOH, Δ, 16 h, 55% for **4a**, 58% for **4c**.

scale.[9] For our purposes, removal of the chloro functionalities in this compound was necessary since heavy atoms such as chlorine are known to quench luminescence and would thus interfere with the photophysical properties of the pyzphen heterocycle and its corresponding metal complex. After some initial ill-fated attempts such as hydrogenolysis of the chloropyridine with palladium on carbon in acetic acid,[16] it was found that refluxing the 4,7-dichloro-phen in acetic acid in the presence of zinc afforded dechlorinated **1c** in quantitative yield (Scheme 1).[17] Although some difficulties were expected in purifying the product from residual zinc salts, the NMR data for **1c** isolated from this experiment were identical to the reported values[10f] and **1c** was used for the subsequent reactions without further purification.

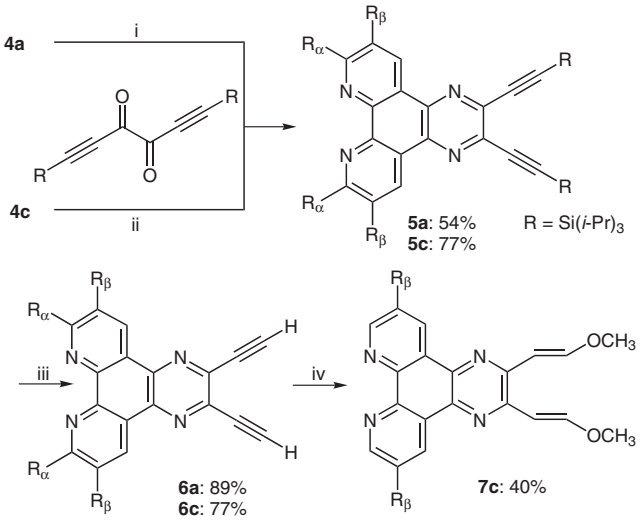
With a number of substituted phen derivatives in hand, their transformation to substituted pyzphens was explored. Hence, **1a–c** were heated separately to reflux in a mixture of concentrated sulfuric and nitric acid in the presence of potassium bromide for two hours.[18] After workup, the butyl-substituted phen-5,6-diones **2a** and **2c** could be isolated as yellow solids in 95% and 74% yield, respectively (Scheme 2). Both compounds were found to be considerably more soluble than the parent 1,10-phenanthroline-5,6-dione[18] and could be characterized by NMR spectroscopy. In contrast, no oxidation product of the aryl-substituted phen **1b** could be detected. Presumably, phen **1b** decomposes in undesired electrophilic substitution side reactions on the aryl termini promoted by the rather harsh reaction conditions.

The two successfully prepared butyl-substituted phen-diones **2a** and **2c** could be further elaborated to the corresponding dioximes by refluxing the diones together with hydroxylamine hydrochloride and barium carbonate in ethanol over night.[19] In analogy to the alkylated phen-5,6-diones, the substituted dibutyl-phen-5,6-dioximes **3a**,**c** show an improved solubility compared to that of the non-substituted parent phen-5,6-dioxime. This effect also facilitates the isolation procedure during which the barium salts can easily be removed by an aqueous work-up. The NMR spectra obtained for the dibutyl-phen-5,6-dioximes were found to be rather convoluted due to the presence of *cis*/*trans* isomers around the imine functionalities and possible hydrogen bonding phenomena between the oxime groups. However, the identity of the compounds could be unambiguously established by mass spectrometry and IR spectrophotometry.

Reduction of the dibutyl-substituted dioximes **3a**,**c** proceeded smoothly by refluxing a solution of the dioximes in ethanol over night in the presence of hydrazine and 10% palladium on carbon. After removal of the palladium catalyst by filtration through Celite, the phen-5,6-diamines **4a**,**c** were isolated as dark brown solids. The solubilizing effect of the two butyl substituents became apparent again as the phen-5,6-diamines **4a**,**c** were found to dissolve readily in polar organic solvents. This fact not only facilitates the acquisition of NMR data, but is also an encouraging prospect with regard to the solubility behavior of the targeted pyzphen heterocycles.

To elaborate **4a**,**c** to terminally free, acetylenic pyzphen ligands, they were condensed with the $(i\text{-Pr})_3$Si-terminated hexa-1,5-diyne-3,4-dione[20] in refluxing toluene in the presence of molecular sieves to obtain **5a** and in acetic acid to afford **5c**. The pyzphens **5a**,**c** were obtained in modest to good yields after chromatographic purification on silica (Scheme 3). Subsequent treatment of **5a**,**c** with tetrabutylammonium fluoride (TBAF) in wet THF resulted in the removal of the silyl protecting groups, liberating the terminal 2,3-diacetylenic pyzphens **6a**,**c**.

Much to our satisfaction, dibutyl-substituted **6a** and **6c**, unlike their non-butylated counterparts, were found to exhibit good solubility in most organic solvents. The butyl substituents, attached either in the α or in the β positions to the phen nitrogens impose a sufficient steric bulk to prevent the pyzphen core from π-stacking. Having obtained a soluble pyzphen ligand with two terminally free acetylene units for the first time, we set out to explore its chemistry. In an initial study, a solution of **6c** in methanol and pyridine was exposed to the copper-mediated acetylene cross-coupling conditions developed by Eglinton.[21] The outcome of this experiment was quite unexpected. After washing the crude reaction mixture with aqueous cyanide to remove the copper from the phen binding site, and purification of the residual material by column chromatography, no butadiynyl-linked product but rather the bis-enolether **7c** was isolated in modest yield. The product



Scheme 3 *Reagents and conditions:* (i) Molecular sieves, toluene, Δ, 2 h, 54% for **5a**. (ii) AcOH, r.t., 1 h, 77% for **5c**. (iii) TBAF, wet THF, 0 °C, 5 min, 89% for **6a**, 77% for **6c**. (iv) 1) CuCl, pyridine, MeOH, 30 min; 2) $Cu(OAc)_2$, 40 °C, 3 h; 3) aq KCN, sonication, 40%.

possesses *trans* configuration across both double bonds as demonstrated by the coupling constant of 12.1 Hz between the two magnetically inequivalent alkene protons. Apparently, the ynimine moieties of the ethynylpyrazine unit in pyzphens of type **6** constitute Michael acceptors and as such are prone to nucleophilic attack on the β carbon of the acetylene. Presumably, the temporary coordination of the copper cation to the phen binding site further increases the electrophilicity of these carbon centers.

In conclusion, the successful realization of soluble acetylenic pyzphens, combined with the nucleophilic properties of the two ynimine subunits, open the way to a new chemistry based on these structural motives. Synthetic work along these lines is currently in progress.

All reactions were conducted in oven-dried glassware under an argon atmosphere. Unless otherwise indicated, all reagents were purchased from commercial suppliers and were used without further purification. 2,9-Disubstituted-1,10-phenanthrolines **1a**,**b**,[14] 3,8-dibutyl-4,7-dichloro-1,10-phenanthroline[9] and 1,6-bis(triisopropylsilyl)hexa-1,5-diyne-3,4-dione[20] were prepared according to the literature procedures. All compounds presented herein were pure by NMR analysis. Due to the hygroscopic nature of the phen-based derivatives, further characterization of key compounds was performed by high-resolution mass spectrometry (HRMS) rather than by elemental analysis. Flash column chromatography was performed under positive pressure from a compressed air line using either silica 60 (supplied by BDH: 230–400 mesh) or neutral Al_2O_3 (Fluka). Melting points were determined on a Reichert hotstage apparatus and are uncorrected. NMR spectra were recorded on a Bruker AMX400 machine in $CDCl_3$ or DMSO-d_6. The chemical shift is given in units of δ relative to the resonances of the residual protic solvent. IR spectra were recorded on a Perkin Elmer 1600 FT-IR instrument either as KBr discs, or in CH_2Cl_2 solution. UV spectra were taken on a Perkin Elmer Lambda 40 instrument. Extinction coefficients ε are given in units of $M^{-1}\cdot cm^{-1}$. Mass spectra were recorded on a VG ZAB SE machine (EI and FAB ionization). Microanalyses were carried out on a Perkin Elmer 2400 CHN machine.

3,8-Dibutyl-1,10-phenanthroline (1c)

Zinc powder (5.2 g, 7.95 mmol) was added to a solution of 3,8-dibutyl-4,7-dichloro-1,10-phenanthroline (1.47 g, 4.07 mmol) in wet AcOH (40 mL). After refluxing for 3 d, the reaction mixture was poured onto ice (50 g) before $CHCl_3$ (50 mL) was added. After adjusting the pH to 14 by the addition of 10 M aq NaOH, the layers were separated. The aqueous layer was extracted with $CHCl_3$ (2 × 50 mL) and the combined extracts were dried (Na_2SO_4), filtered and concentrated in vacuo.

Yield: 1.19 g (4.07 mmol, quant.). The spectroscopic data are in agreement with the reported values.[10f]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.98 (d, *J* = 2.2 Hz, 2 H, α CH), 7.96 (d, *J* = 2.2 Hz, 2 H, γ CH), 7.69 (s, 2 H, phen), 2.84 (t, *J* = 7.6 Hz, 4 H, CH_2), 1.72 (m, 4 H, CH_2), 1.40 (m, 4 H, CH_2), 0.95 (t, *J* = 7.3 Hz, 6 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.4, 144.6, 137.2, 134.4, 128.0, 126.3 (all aromatic C), 33.3, 32.8, 22.3, 13.9 (Bu).

2,9-Dibutyl-1,10-phenanthroline-5,6-dione (2a)

2,9-Dibutylphenanthroline (1.46 g, 5.00 mmol) and KBr (5.95 g, 50 mmol) were placed in an ice-cooled one-neck flask and ice-cooled concd H_2SO_4 (20 mL) was added carefully along the wall of the flask. Concd HNO_3 (10 mL) was added and the fuming reaction mixture was refluxed for 2 h. After cooling to r.t., the red solution was poured onto ice-cold H_2O (400 mL) and neutralized by careful addition of $NaHCO_3$. The yellow solution was extracted with CH_2Cl_2 (5 × 70 mL), the combined organic layers were washed with brine (100 mL), dried (Na_2SO_4), filtered and concentrated in vacuo.

Yellow solid; yield: 1.53 g (4.75 mmol, 95%); mp 86 °C.

IR (KBr): 3066 (CH), 2957 (CH), 1692 cm^{-1} (C=O).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.34 (d, *J* = 8.0 Hz, 2 H, γ CH), 7.37 (d, *J* = 8.0, 2 H, β CH), 3.06 (t, *J* = 8.0 Hz, 4 H, CH_2), 1.83 (m, 4 H, CH_2), 1.46 (m, 4 H, CH_2), 0.97 (t, *J* = 7.3 Hz, 6 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.1 (C=O), 171.0, 152.7, 137.3, 126.1, 124.4 (all aromatic C), 39.0, 31.2, 22.6, 13.9 (aliphatic C).

3,8-Dibutyl-1,10-phenanthroline-5,6-dione (2c)

Synthesized from 3,8-dibutyl-1,10-phenanthroline (1.19 g, 4.07 mmol) in a procedure similar to the one used for the preparation of **2a**.

Yellow solid; yield: 970 mg (3.00 mmol, 74%); mp 140 °C (dec.).

IR (CH_2Cl_2): 2956 (CH), 2930 (CH), 2860 (CH), 1687 cm^{-1} (C=O).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (d, *J* = 2.2 Hz, 2 H, α CH), 8.20 (d, *J* = 2.2 Hz, 2 H, γ CH), 2.71 (t, *J* = 7.8 Hz, 4 H, CH_2), 1.63 (m, 4 H, CH_2), 1.35 (m, 4 H, CH_2), 0.90 (t, *J* = 7.3 Hz, 6 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.1 (C=O), 156.6, 150.8, 140.5, 136.4, 127.2 (all aromatic C), 32.6, 32.3, 22.1, 13.7 (Bu).

MS (FAB): *m*/*z* (%) = 323 (100) [M^+ + H].

2,9-Dibutyl-1,10-phenanthroline-5,6-dioxime (3a)

A suspension of **2a** (644 mg, 2.00 mmol), hydroxylamine hydrochloride (486 mg, 7 mmol) and $BaCO_3$ (592 mg, 3.00 mmol) in EtOH (30 mL) was heated to reflux for 12 h. After removal of the solvent, the residue was triturated with 0.2 M HCl (40 mL) for 1 h. The suspension was extracted with CH_2Cl_2 (3 × 50 mL) and the combined extracts were washed with brine (30 mL), dried (Na_2SO_4), filtered and concentrated in vacuo.

Yield: 450 mg (1.28 mmol, 64%); mp 145 °C.

IR (KBr): 2957 (CH), 2866 (CH), 1583 cm^{-1} (C=NOH).

MS (FAB): *m*/*z* (%) = 352 (100) [M^+].

3,8-Dibutyl-1,10-phenanthroline-5,6-dioxime (3c)
Synthesized from **2c** (969 mg, 3.00 mmol) in a procedure similar to the one used for the preparation of **3a**.

Yield: 765 mg (2.17 mmol, 72%); mp 158 °C.

IR (KBr): 2956 (CH), 2929 (CH), 2859 (CH), 1560 cm^{-1} (C=NOH).

MS (FAB): *m*/*z* (%) = 353 (100) [M^+ + H], 335 (87) [M^+ + H – H_2O].

HRMS (FAB): *m*/*z* [M^+ + H] calcd for $C_{20}H_{25}N_4O_2$: 353.1978; found: 353.1960.

2,9-Dibutyl-1,10-phenanthroline-5,6-diamine (4a)
A suspension of **3a** (352 mg, 1.00 mmol) and palladium on charcoal (10%, 300 mg) in anhyd EtOH (50 mL) was purged with argon for 15 min and heated to reflux. A solution of hydrazine-monohydrate (1.75 mL, 36.00 mmol) in anhyd EtOH (15 mL) was added over a period of 30 min. After refluxing for 16 h the hot reaction mixture was filtered through a pad of Celite and washed with boiling EtOH (4 × 15 mL). After removal of the solvent in vacuo the remaining black residue was triturated with H_2O (15 mL), stored at 4 °C for 2 h and collected.

Yield: 177 mg (0.55 mmol, 55%); mp 188 °C.

IR (KBr): 3355 (NH), 3228 (NH), 2956 (CH), 2928 cm^{-1} (CH).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.40 (d, *J* = 8.7 Hz, 2 H, γ CH), 7.49 (d, *J* = 8.7 Hz, 2 H, β CH), 2.94 (t, *J* = 7.9 Hz, 4 H, CH_2), 1.71 (m, 4 H, CH_2), 1.37 (m, 4 H, CH_2), 0.90 (t, *J* = 7.3 Hz, 6 H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 156.7, 139.1, 129.7, 121.8, 121.6, 121.1 (all aromatic C), 37.4, 31.8, 22.2, 13.9 (aliphatic C).

MS (FAB): *m*/*z* (%) = 323 (100) [M^+ + H].

HRMS (FAB): *m*/*z* [M^+ + H] calcd for $C_{20}H_{27}N_4$: 323.2236; found 323.2234.

3,8-Dibutyl-1,10-phenanthroline-5,6-diamine (4c)

Synthesized from **3c** (352 mg, 1.00 mmol) in a procedure similar to the one used for the preparation of **4a**.

Yield: 188 mg (0.58 mmol, 58%); mp 156 °C.

IR (KBr): 2956 (CH), 2927 (CH), 2858 cm^{-1} (CH).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.59 (d, *J* = 2.2 Hz, 2 H, α CH), 8.24 (d, *J* = 2.2 Hz, 2 H, γ CH), 5.13 (br s, 4 H, NH_2), 2.79 (t, *J* = 7.9 Hz, 4 H, CH_2), 1.70 (m, 4 H, CH_2), 1.37 (m, 4 H, CH_2), 0.97 (t, *J* = 7.3 Hz, 6 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.8, 139.4, 135.5, 127.1, 122.1, 121.8 (all aromatic C), 33.0, 32.4, 21.9, 13.8 (Bu).

HRMS (FAB): *m*/*z* [M^+ + H] calcd for $C_{20}H_{27}N_4$: 323.2236; found: 323.2250.

7,10-Dibutyl-2,3-bis[(triisopropylsilyl)ethynyl]pyrazino [2,3-*f*]-1,10-phenanthroline (5a)
To a solution of **4a** (161 mg, 0.50 mmol) in toluene (15 mL) over activated molecular sieves was added a solution of 1,6-bis(triisopropylsilyl)hexa-1,5-diyne-3,4-dione (210 mg, 0.50 mmol) in toluene (10 mL) and the reaction was stirred at 100 °C for 2 h. After removal of the molecular sieves, the solvent was removed in vacuo to afford a brown solid which was subjected to column chromatography (alumina, 20% EtOAc in hexane) to furnish a hygroscopic, off-white solid.

Yield: 190 mg (0.27 mmol, 54%); mp 74 °C.

IR (CH_2Cl_2): 2962 (CH), 2945 (CH), 2151 cm^{-1} (C≡C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.32 (d, *J* = 8.3 Hz, 2 H, γ CH), 7.62 (d, *J* = 8.3 Hz, 2 H, β CH), 3.21 (m, 4 H, CH_2), 1.92 (m, 4 H, CH_2), 1.50 (m, 4 H, CH_2), 1.20 (m, 42 H, *i*-Pr), 0.90 (t, *J* = 7.4 Hz, 6 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.0, 147.2, 139.3, 138.0, 133.8, 124.3, 123.2 (all aromatic C), 103.7, 99.3 (C≡C), 39.1, 31.7, 22.8 (aliphatic C), 18.7 [$CH(CH_3)_2$], 14.0 (aliphatic C), 11.3 (Si–C).

HRMS (FAB): *m*/*z* [M^+ + H] calcd for $C_{44}H_{65}N_4Si_2$: 705.4748; found: 705.4776.

UV (CH_2Cl_2): λ_{max} (ε) = 282 (60000), 319 (24000), 389 nm (23000).

6,11-Dibutyl-2,3-bis[(triisopropylsilyl)ethynyl]pyrazino-[2,3-*f*]-1,10-phenanthroline (5c)
Compound **4c** (97 mg, 0.30 mmol) was added in one portion to a deoxygenated solution of 1,6-bis(triisopropylsilyl)hexa-1,5-diyne-3,4-dione (126 mg, 0.30 mmol) in glacial AcOH (10 mL). After stirring for 1 h, the solvent was removed at high vacuum and the remaining red residue was purified by column chromatography (silica, 5% MeOH in CH_2Cl_2) and recrystallized from MeOH, white solid.

Yield: 164 mg (0.23 mmol, 77%); mp 60 °C.

IR (KBr): 2941 (CH), 2891 (CH), 2158 cm^{-1} (C≡C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.12 (d, *J* = 2.2 Hz, 2 H, γ CH), 8.99 (d, *J* = 2.2 Hz, 2 H, α CH), 2.89 (t, *J* = 7.6 Hz, 4 H, CH_2), 1.73 (m, 4 H, CH_2), 1.40 (m, 4 H, CH_2), 1.18 (m, 42 H, *i*-Pr), 0.98 (t, *J* = 7.3 Hz, 6 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.3, 145.8, 139.4, 138.4, 138.2, 132.3, 125.4 (all aromatic C), 103.6, 99.9 (both C≡C), 33.1, 32.8, 22.2 (all Bu), 18.7 [$CH(CH_3)_2$], 13.8 (Bu), 11.0 (CH).

MS (EI): *m*/*z* (%) = 705 (38) [M^+], 661 (65) [M^+ – *i*-Pr], 619 [M^+ – 2 *i*-Pr].

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{44}H_{65}N_4Si_2$: 705.4748; found 705.4730.

UV (CH_2Cl_2): λ_{max} (ε) = 280 (60000), 317 (27000), 359 (12000), 367 (16000), 378 (15000), 386 nm (22000).

Anal. Calcd for $C_{44}H_{64}N_4Si_2 \cdot 0.5H_2O$: C, 74.0; H, 9.1; N, 7.8. Found: C, 74.1; H, 9.0; N, 7.9.

7,10-Dibutyl-2,3-diethynylpyrazino[2,3-*f*]-1,10-phenanthroline (6a)
Tetrabutylammonium fluoride (1.5 mL, 1.5 mmol, 1 M soln in THF) was added to a degassed solution of compound **5a** (352 mg, 0.50 mmol) in wet THF (20 mL) at 0 °C. After stirring for 5 min the reaction was quenched by the addition of a sat. aq solution of NH_4Cl (20 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic extracts were washed with brine (30 mL) and dried (Na_2SO_4). Purification by column chromatography (alumina, 10% EtOAc in hexane), white solid.

Yield: 174 mg (0.44 mmol, 89%); mp 137 °C.

IR (CH_2Cl_2): 2961 (CH), 2931 (CH), 2117 cm^{-1} (C≡C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.32 (d, *J* = 8.3 Hz, 2 H, γ CH), 7.63 (d, *J* = 8.3 Hz, 2 H, β CH), 3.64 (s, 2 H, acetylenic H), 3.21 (m, 4 H, CH_2), 1.91 (m, 4 H, CH_2), 1.50 (m, 4 H, CH_2), 0.96 (t, *J* = 7.4 Hz, 6 H, CH_3).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.6, 147.3, 139.2, 138.6, 133.8, 123.9, 123.4 (all aromatic C), 83.8, 80.2 (C≡C), 39.1, 31.7, 22.8, 14.0 (aliphatic C).

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{25}N_4$: 393.2079; found 393.2062.

UV (CH_2Cl_2): λ_{max} (ε) = 275 (53000), 381 nm (19000).

6,11-Dibutyl-2,3-diethynylpyrazino[2,3-*f*]-1,10-phenanthroline (6c)

Synthesized from **5c** (176 mg, 0.25 mmol) in a procedure similar to the one used for the preparation of **6a**. Purification by column chromatography (silica, 3% MeOH in CH_2Cl_2), white solid.

Yield: 76 mg (0.19 mmol, 77%); mp 160 °C.

IR (KBr): 3221 (C≡CH), 2954 (CH), 2927 (CH), 2859 (CH), 2104 cm^{-1} (C≡C).

^1H NMR (400 MHz, $CDCl_3$): δ = 9.13 (d, *J* = 2.2 Hz, 2 H, γ CH), 9.03 (d, *J* = 2.2 Hz, 2 H, α CH), 3.65 (s, 2 H, C≡CH), 2.88 (t, *J* = 7.9 Hz, 4 H, CH_2), 1.74 (m, 4 H, CH_2), 1.41 (m, 4 H, CH_2), 0.94 (t, *J* = 7.3 Hz, 6 H, CH_3)

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 153.8, 146.0, 139.4, 138.9, 138.8, 132.3, 125.1 (all aromatic C), 84.1, 80.0 (both C≡C), 33.4, 33.0, 22.3, 13.8 (all Bu).

HRMS (FAB): *m/z* $[M + Na]^+$ calcd for $C_{26}H_{24}N_4Na$: 415.1899; found: 415.1904.

UV (CH_2Cl_2): λ_{max} (ε) = 274 (52000), 319 (23000), 351 (11000), 359 (13000), 369 (10000), 377 nm (15000).

6,11-Dibutyl-2,3-bis[(*E*)-2-methoxyvinyl]pyrazino[2,3-*f*]-1,10-phenanthroline (7c)

CuCl (85 mg, 0.86 mmol) was added to a degassed solution of **6c** (48 mg, 0.12 mmol) in MeOH and pyridine (1:1, 100 mL) and $Cu(OAc)_2 \cdot H_2O$ (171 mg, 0.86 mmol) was added at 40 °C. After 3 h at this temperature, a degassed solution of KCN (1.1 g, 16.90 mmol) in H_2O (5 mL) was added. Sonication for 1 h was followed by removal of the solvents in vacuo. The residue was filtered through a plug of silica (eluent: 10% MeOH in CH_2Cl_2) and further purified by column chromatography (silica, 4% MeOH in CH_2Cl_2).

Yield: 22 mg (0.05 mmol, 40%); mp 94 °C.

IR (CH_2Cl_2): 2961 (CH), 2932 (CH), 2860 (CH), 1626 cm^{-1} (C=C).

^1H NMR (400 MHz, $CDCl_3$): δ = 9.10 (d, *J* = 2.0 Hz, 2 H, γ CH), 8.99 (d, *J* = 2.0 Hz, 2 H, α CH), 8.03 (d, *J* = 12.1 Hz, 2 H, HC=C), 6.18 (d, *J* = 12.1 Hz, 2 H, C=CH), 3.89 (s, 6 H, OCH_3), 2.91 (t, *J* = 7.7 Hz, 4 H, CH_2), 1.77 (m, 4 H, CH_2), 1.44 (m, 4 H, CH_2), 0.97 (t, *J* = 7.4 Hz, 6 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.9, 152.1, 147.2, 145.2, 137.9, 136.9, 131.2 (all aromatic C), 126.6, 99.9 (C=C), 57.6 (OCH_3), 33.5, 33.1, 22.4, 13.9 (all Bu).

HRMS (FAB): *m/z* $[M + H]^+$ calcd for $C_{28}H_{33}N_4O_2$: 457.2604; found: 457.2620.

Acknowledgment

This work was supported by the Engineering and Physical Sciences Research Council UK (Grant No. GR/N09503). We wish to acknowledge a UCL Provost studentship to S.O.

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