Heterocyclic free radicals. Part 1. 4,5-Diazafluorene derivatives of Koelsch's free radical: an EPR and metal-ion complexation study †

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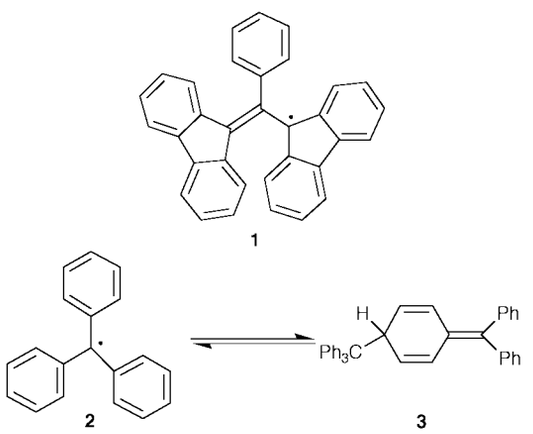
Heteroaromatic precursors to nitrogen substituted derivatives of Koelsch's free radical have been prepared by the condensation of 4,5-diazafluorene with a fluorenylidene or diazafluorenylidene. These compounds appear coloured and can exist in different tautomeric forms. An improved one pot synthesis of 4,5-diazafluorenone has been developed by the oxidative ring contraction of 1,10-phenanthroline with aqueous potassium permanganate. Aza derivatives of Koelsch's free radical are easily generated by oxidation of the appropriate precursors with $K_3Fe(CN)_6$. Treatment of 9-[(9*H*-4,5-diazafluoren-9-ylidene)phenylmethyl]-9*H*-fluoren-9-yl radical with $CuCl_2$ in EtOH gives a brown precipitate of a 1 : 1 radical–ligand complex.

Koelsch's free radical **1**, first reported in 1957, is remarkably



stable for a free radical considering that it is not substituted with alkyl or halo groups to increase the steric hindrance.[1,2] It is monomeric in solution and in the solid state[3] which contrasts with the properties of triphenylmethyl radical **2** which occurs as a dissociating dimer **3**.[4] Koelsch's free radical **1** shows good stability to oxygen in refluxing benzene and can be recrystallised successfully without special anaerobic conditions. A later study however showed that slow absorption of oxygen takes place which suggests that in benzene reaction of the radical with oxygen may occur but is probably reversible.[5] The absence of a hydrogen source prevents abstraction of hydrogen by a peroxy-radical intermediate. The stability of radical **1** compared to trityl radical **2** can be attributed to greater resonance delocalisation and probably greater steric hindrance owing to the bulk of two fluorenyl groups compared to benzene rings.

We report in this paper the synthesis of nitrogen substituted derivatives of Koelsch's free radical **1** which were prepared to study their stability, EPR spectra and the formation of metal-ion complexes. The beautiful symmetry of this molecule and delocalisation of the radical onto both fluorene groups make its aza derivatives interesting potential building blocks for supramolecular assemblies. Also very few studies have been carried out on aza-aromatic type free radicals. A recent EPR and ENDOR study of diphenyl(2-, 3- or 4-pyridyl)methyl radicals **4**, **5** and **6** respectively,[6] showed that the radicals are similar in structure or shape to the parent trityl free radical **2**. The EPR spectra were complex because of the 1 : 1 : 1 nitrogen splitting and the extra coupling constants arising from the unsymmetrical nature of the molecule. They formed dimers exclusively through the pyridine ring. The bond dissociation enthalpies of the dimers, determined using EPR spectroscopy, showed strengthening of the central C–C bond in **4** (88.7 kJ mol^{-1}) and **5** (90.0 kJ mol^{-1}) but a similar value for **6** (46.4 kJ mol^{-1}) with respect to the trityl dimer (44.8 kJ mol^{-1}). This was attributed to the relief of steric strain in the dimers formed from radicals **4** and **5** owing to the lower steric demand of a nitrogen atom *versus* a C–H bond. For **6** the weaker C–N dimer bond compensates for this. Pyridine rings have less aromatic stabilisation energy than benzene rings which would also favour dimerisation. It was of interest to see if diaza derivatives of Koelsch's free radical would remain essentially monomeric or display a tendency to dimerise for similar reasons.

Results and discussion

4,5-Diazafluorene derivatives of Koelsch's free radical **23**, **24** and **25** were prepared by Neugebauers route[2] (shown in Scheme 2). 4,5-Diazafluoren-9-one **11** is a key building block which has been exploited for the synthesis of rigid scaffolds to study excited state decay pathways of the corresponding ruthenium(II) complexes.[7] These are of interest for the development of solar energy conversion devices and for the assembly of monolayers.[8] 4,5-Diazafluoren-9-one **11** can be prepared by the one step oxidative ring contraction of phenanthroline[9] **7** as shown in Scheme 1. Following the literature conditions in our hands the yield of about 20% was too low to allow ready access to multigram quantities. The main unwanted by-product is 2,2′-bipyridyl-3,3′-dicarboxylic acid **13** which forms *via* oxidation of 1,10-phenanthroline-5,6-quinone **8**. The desired reaction pathway requires a rapid benzil-benzilic acid ring contraction of quinone **8** so we reasoned that increasing the concentration of alkali and adding a dilute solution of $KMnO_4$ more slowly would favour the ring contraction. By doubling the initial concentration of aqueous alkali from 0.12 M to 0.24 M (20 g of KOH in 1.5 l of H_2O) the yield of 4,5-diazafluoren-9-one **11** increased to 55–60%. Starting from 20 g of commercial phenanthroline, 10–12 g of product **11** can now be routinely

† EPR spectra of **26**–**28**, **33** and **34** are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p1/a9/a909109b/

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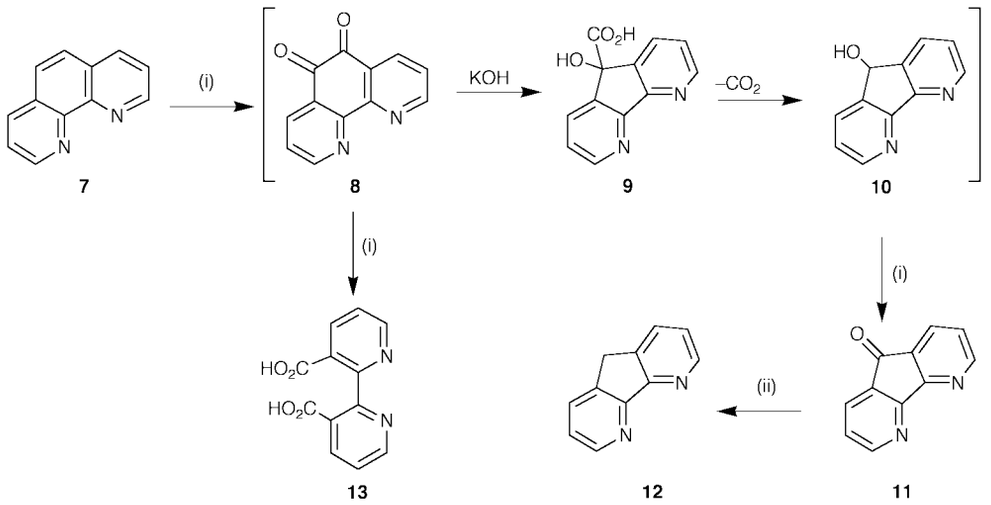
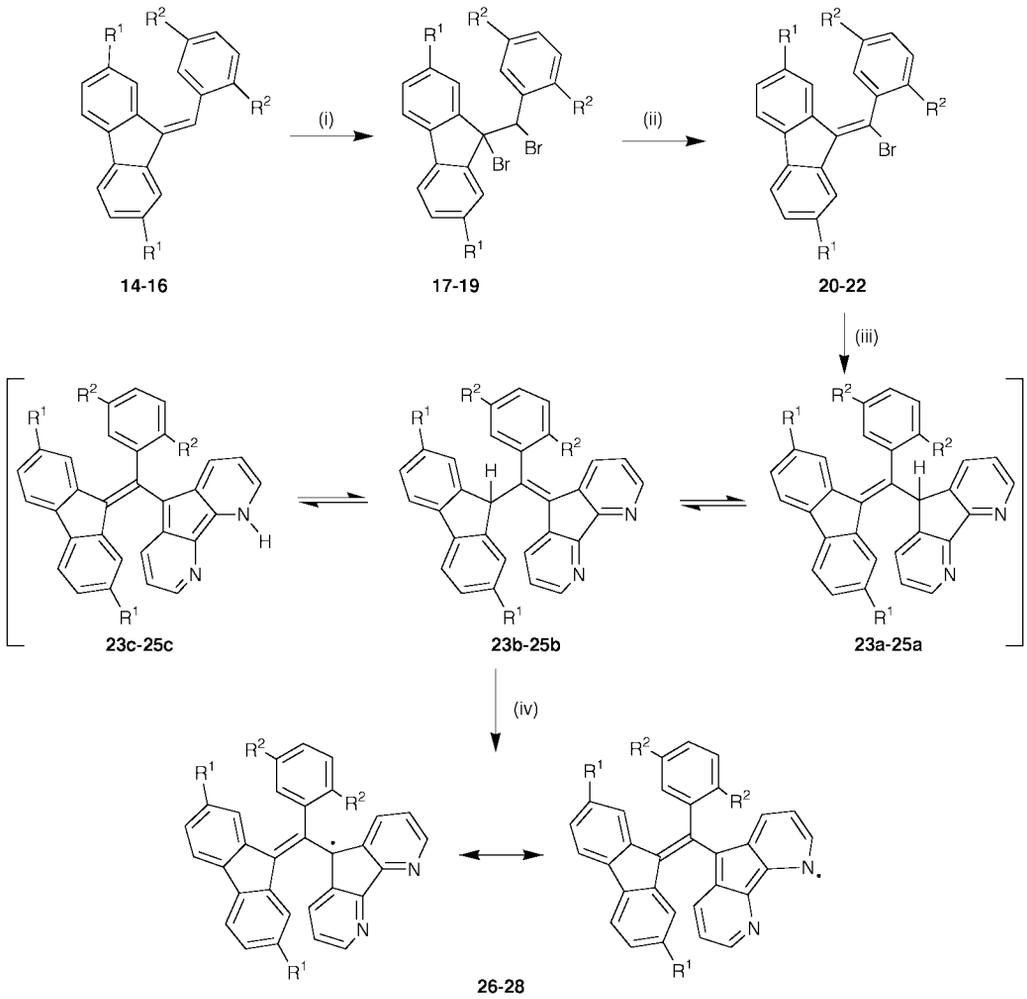


Scheme 1 *Reagents and conditions*: (i) $KMnO_4$, 0.24 M aq. KOH, Δ; (ii) NH_2NH_2, Δ, Parr bomb.

obtained making this key intermediate readily accessible. The synthetic route shown in Scheme 2 involves condensation of fluorene or 2,7-dibromofluorene with either benzaldehyde or 2,5-dimethylbenzaldehyde, bromination and subsequent elimination of HBr in hot acetic acid to give Michael acceptors **20**, **21** and **22**. In compounds **17**–**19** the two halves of the fluorene ring are in different chemical environments because of the chiral centre that is present. Treatment of **20**, **21** and **22** with 4,5-diazafluorene **12** and base gave the precursors **23**, **24** and **25**. The synthesis of the symmetrical derivatives **31** and **32** proceeded in a similar manner starting by aldol condensation of 4,5-diazafluorene **12** with either benzaldehyde or 2,5-dimethylbenzaldehyde to give **29** and **30** respectively (Scheme 3). Subsequent treatment with 4,5-diazafluorene and base in the presence of air gives precursors **31** and **32** by Michael addition followed by *in situ* oxidation. Free radical precursors **23**, **24**, **25**, **31** and **32** are all a deep purple colour, which contrasts with the pale yellow colour of the hydrocarbon precursor **35** to Koelsch's free radical **1**. The UV spectra all show a long wavelength absorption with λ_{max} values in the range 480–535 nm which is absent for hydrocarbon **35**. The compounds **23**, **24** and **25** can exist as a mixture of three different tautomers (**a**,**b**,**c**). Tautomers **a** and **b** are similar in structure to **35** and should be colourless or pale yellow coloured. However tautomer **c**, in which the nitrogen is protonated, is a push-pull chromophore and accounts for the purple colour. The long wavelength λ_{max} values for compounds **23**, **24** and **25** are 480, 534 and 520 nm respectively. The bromines in compound **24** cause a bathochromic shift of 54 nm by increasing the electron withdrawal of the fluorene group. Substitution of the central phenyl ring with an *ortho* methyl group causes a slight hypsochromic shift of 15 nm probably owing to decreased conjugation as a consequence of enhanced molecular twisting. The tetra-aza derivatives **31** and **32** have long wavelength λ_{max} values at 533 (shoulder at 560 nm) and at 575 nm. The bathochromic shift of the λ_{max} values is attributed to the stronger push-pull conjugation present.

The precursors require careful purification and handling because atmospheric autooxidation to the corresponding free radical occurs readily. TLC analysis of samples left in air showed the presence of the corresponding radical as a faster running brown spot. Addition of a small quantity of ascorbic acid to a solution of the precursor prior to TLC analysis caused the disappearance of this spot. Autooxidation frequently complicated the acquisition of NMR data by causing considerable line broadening and significant weakening of the observed resonances. The compounds occurred as amorphous powders and repeated attempts at recrystallisation were unsuccessful. Nevertheless, despite considerable difficulties in purification, after careful chromatography satisfactory ^1H and ^{13}C spectra were recorded. The spectra were complex indicating the presence of a mixture of tautomers although some spectroscopic features are noteworthy. Compound **23** showed two strong singlets at 6.3 and 6.4 ppm in a 2 : 1 ratio. These are assigned to the aliphatic protons which occur at 6.45 ppm in precursor **35**. A broad resonance, which disappeared after a D_2O shake, was present at 5.2–5.8 ppm. In a separate run the spectrum was identical except that this peak occurred at 4.5 ppm suggesting that the chemical shift was concentration dependent. This could be explained if the molecules could self-associate by forming hydrogen bond dimers analogous to the formation of carboxylic acid dimers. The presence of minor overlapping peaks made an accurate determination of the integral difficult but, despite the intense purple colour, it appeared to be a minor tautomer of the mixture. The D_2O shake did not diminish the intensity of the aliphatic protons which suggested that the tautomers are not interconverting. The ^{13}C spectrum was well resolved and showed two peaks at 49 and 54 ppm assigned to the aliphatic carbons of tautomers **23a** and **23b**. The peak at 54 ppm was more intense. In the aromatic range 120–165 ppm 47 peaks were present. A mixture of the three tautomers **23a**–**c** should give a total of 74 peaks (23 + 22 + 29), respectively, in this region assuming that the protonated diazafluorene ring is asymmetric. In a separate run the ^{13}C DEPT 135 spectrum, showing carbons substituted with one hydrogen, clearly showed 26 aromatic resonances which is close to the expected number of resonances for a mixture of the two tautomers **23a** and **23b** (14 + 13 peaks respectively). These NMR data suggest that only two main tautomers are present which are tentatively assigned as **23a** and **23b**. The coloured tautomer **23c** is clearly present but presumably as a sufficiently low percentage of the mixture that its ^{13}C spectrum has not been resolved from the baseline. The ^1H NMR spectrum of compound **25** showed 4 strong aliphatic resonances owing to the methyl groups at 1.84, 1.91, 2.81 and 2.88 ppm. This suggests again that either two predominant tautomers are present or that the compound exists as diastereomers. The best explanation is that tautomers **25a** and **25b** predominate while the chromophore **25c** is a minor component of the mixture. The symmetric tetra-aza compounds **31** and **32** should be more acidic and might be more stable as the corresponding coloured chromophore. Compound **31** showed two strong methyl group signals in the ^1H NMR spectrum at 1.87 and 1.90 ppm suggesting that only one predominant tautomer was observed. The long wavelength UV/VIS λ_{max} extinction coefficients, $\varepsilon = 16\,980$ and 19 500 for **31** and **32** respectively, are more intense by a factor of four compared to the unsymmetric compounds **23**–**25**. Despite repeated attempts at purification it was not possible to con-



Compound	R^1	R^2	Yield (%)
14	H	H	73
15	Br	H	83
16	Br	Me	83
17	H	H	89
18	Br	H	85
19	Br	Me	68
20	H	H	76
21	Br	H	69
22	Br	Me	82
23	H	H	43
24	Br	H	45
25	Br	Me	87
26	H	H	88
27	Br	H	43
28	Br	Me	43

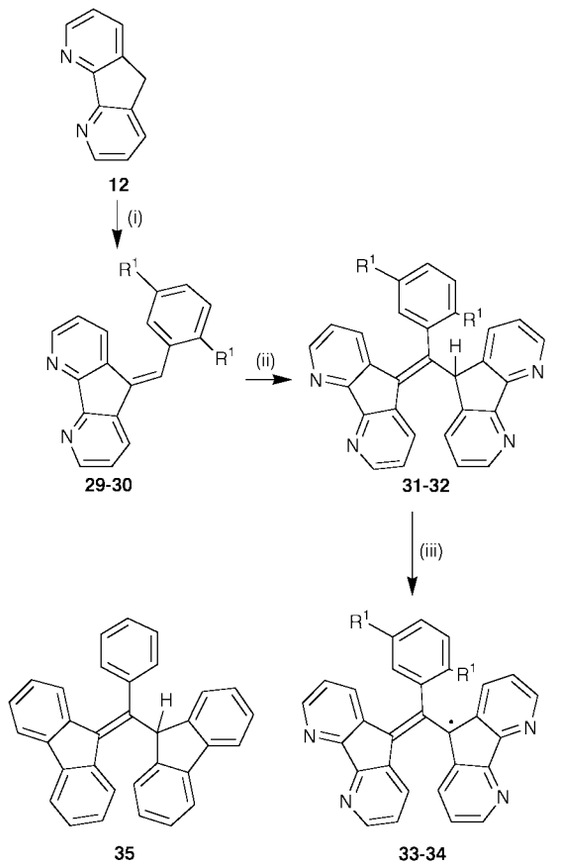
Scheme 2 *Reagents and conditions*: (i) Br_2, HOAc; (ii) HOAc, Δ; (iii) 4,5-diazafluorene, ^{t}BuOK; (iv) ^{t}BuOK, DMF, $K_3Fe(CN)_6$.

clude which tautomer predominated. All the precursors **23**, **24**, **25**, **31** and **32** gave strong molecular ions in the mass spectrum and satisfactory microanalytical data were obtained for some compounds despite the difficulties encountered in purification and in obtaining NMR data.

The acquisition of NMR data for the corresponding anions was easily achieved. They were formed by treatment with ^{t}BuOK in DMSO-d_6. The anions are more soluble, probably as a consequence of their inability to form hydrogen bonds. They exist as only one resonance species and have greater symmetry. The NMR spectra were greatly simplified and easier to interpret. The ^{13}C spectra in particular were beautifully resolved for each anion. For example in the spectrum of the symmetric tetra-aza anion **32a** there was the expected number of 11 peaks while tetra-aza anion **31a** showed 14 of the expected 15 peaks. Two signals for the methyl groups occurred at 18.8 and 20.6 ppm.

Generation of poly-aza free radicals

Precursors **23**, **24**, **25**, **31** and **32** were easily oxidised to the corresponding free radicals **26**, **27**, **28**, **33** and **34** by treatment with ^{t}BuOK–$K_3Fe(CN)_6$ in aqueous DMF followed by precipitation with water. Satisfactory microanalytical data could not be obtained indicating that the radicals were not isolated in a pure state under these conditions. The radicals are brown and lack the long wavelength UV absorption present in the precursors. No dimeric products were detected or isolated



Compound	R^1	Yield (%)
29	H	81
30	Me	95
31	H	20
32	Me	20
33	H	77
34	Me	76

Scheme 3 *Reagents and conditions*: (i) KOH, BnOH, PhCHO or 2,5-DiMePhCHO; (ii) diazafluorene **12**, ^{t}BuOK, air; (iii) $K_3Fe(CN)_6$, ^{t}BuOK.

suggesting that they are highly dissociated like Koelsch's free radical. The EPR spectrum for each radical measured in toluene showed a single broad unresolved resonance with line widths in the range 6.08–6.71 G. The EPR spectrum of Koelsch's free radical (5.3×10^{-3} M) was similar but with a narrower line width of 3.40 G.[10] Dilution of the radicals had no effect on the resolution of the spectra and so the line broadening is not due to an exchange interaction between the radicals. The *g*-values were calculated to be in the range 2.0023–2.0026 which are similar to the value for Koelsch's free radical of 2.0026. The unsymmetric radicals showed good stability in solution with no noticeable decrease in EPR signal intensity over a period of a few days. The symmetric radical **33** was more reactive and showed a decrease in signal intensity over a period of 1 week. The more hindered radical **34** showed comparable stability to the unsymmetric radicals. The aza derivatives are more chemically reactive than Koelsch's free radical and cannot be purified by column chromatography. On spotting on a TLC plate the radicals abstract hydrogen and show a characteristic spot for both the radical and the starting material. The greater reactivity may be a consequence of the ring nitrogens through which the radical may more readily react with oxygen or hydrogen atom donors. Nevertheless the radicals showed good stability in both chloroform, ethanol and toluene.

Metal-ion complexation studies

Treatment of an ethanolic solution of precursors **23**, **24** and **25** with an ethanolic solution of either Cu(II), Co(II), Ni(II) or Zn(II) gave purple precipitates. The UV spectra indicated the formation of metal complexes owing to the bathochromic shift of the long wavelength absorption by 30–60 nm. The complexes could be analysed by TLC and eluted with CH_2Cl_2 at a different R_f value to the starting ligand. However microanalytical data were variable for each batch of metal complex which suggested that the complexes were either unstable or were a mixture of complexes of different stoichiometry. Treatment of tetradentate ligand **31** or **32** with $Zn(OAc)_2$ gave a purple precipitate which was insoluble in organic solvents. It did not move off the baseline by TLC analysis using MeOH as eluent indicating the formation of polymeric species. The complexes were not characterised in further detail. Mixing the free radical **26** in EtOH with either a solution of $Cu(I)PF_6(CH_3CN)_4$ or $Ag(I)ClO_4$ in EtOH gave no isolable products. The solution of radical with Cu(I) turned from brown to a characteristic purple colour indicating electron transfer from the Cu(I) cation to the ligand generating the ligand anion. The *in situ* formation of the ligand anion and Cu(II) cations must complicate the desired complex formation although the possibility of electron transfer occurring from the Cu(I) cation to the coordinating radical in a 1 : 1 complex cannot be ruled out. However, mixing a solution of the radical **26** in EtOH with a solution of $CuCl_2$ in EtOH gave a brown microcrystalline precipitate which was identified approximately by analysis as a radical–metal-ion 1 : 1 complex. The complex probably contains 2 ligands and 2 Cu cations bridged by chloride ions analogous to the structure of related 4,5-diazafluorene type $CuCl_2$ complexes.[9] Treatment of an ethanolic solution of the symmetrical tetra-aza radical **33** with an ethanolic solution of $CuCl_2$ also gave a brown microcrystalline precipitate which may have a polymeric structure. Attempts to grow crystals suitable for single crystal structure determination by layering a solution of the radical onto a solution of $CuCl_2$ have so far proved unsuccessful. To the best of our knowledge the radical–$CuCl_2$ complexes prepared here are the first metal complexes of a polypyridyl free radical.

Experimental

General

NMR spectra were recorded on either a Bruker AC-250 or a Varian Unity 400 spectrometer; *J* values are quoted in Hz. EPR spectra were measured on a Bruker ECS 106 spectrometer.

9*H*-4,5-Diazafluoren-9-one 11

1,10-Phenanthroline (20 g, 0.11 mol) and KOH (20 g, 0.36 mol) were dissolved in H_2O (1.5 l) and heated to boiling. A hot solution of $KMnO_4$ (50 g, 0.32 mol) in H_2O (800 ml) was then added over 3 h with stirring. On completion of the addition the reaction mixture was boiled for a further 10 min then filtered hot. The orange filtrate was cooled and extracted with chloroform (3 × 500 ml). The combined organic extracts were dried over anhydrous $MgSO_4$ and the solvent removed under reduced pressure. The solid residue was recrystallised to give the *title compound* (11.05 g, 55%) as yellow crystals, mp 218–219 °C (from acetone) (lit.,[11] 214–215 °C); ν_{max}(KBr)/cm^{-1} 3050m, 2995m, 1716s, 1587m, 1555s, 1505m, 1401s, 1276m, 1088m, 915m and 762s; δ_H(250 MHz; $CDCl_3$) 7.33 (2 H, dd, *J* 7.6 and 5.2), 7.96 (2 H, dd, *J* 7.6 and 1.5) and 8.77 (2 H, dd, *J* 5.2 and 1.5); δ_C(62.9 MHz; $CDCl_3$) 124.8, 129.3, 131.5, 155.2, 163.4 and 189.6; *m*/*z* (EI) 183 ($M^+ + 1$, 100%), 168 (3), 155 (7).

9*H*-4,5-Diazafluorene 12

4,5-Diazafluoren-9-one **11** (2.0 g, 11.0 mmol) and hydrazine hydrate (14 ml, 0.29 mol) were heated at 180 °C for 6 h in a Teflon-lined bomb. After cooling, the reaction mixture was

extracted with CH_2Cl_2 (4 × 100 ml) and the combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated to give a solid. Chromatography on silica gel with ethyl acetate as the eluent yielded the *title compound* (1.4 g, 75%) as colourless crystals, mp 170–171 °C (from methanol) (lit.,[12] 172 °C); ν_{max}(KBr)/cm^{-1} 3030m, 2995s, 1567m, 1408s, 1225m, 1161m, 752m and 663m; δ_H(250 MHz; $CDCl_3$) 3.86 (2 H, s), 7.29 (2 H, dd, *J* 4.9 and 7.6), 7.87 (2 H, dd, *J* 0.6 and 7.6) and 8.73 (2 H, dd, *J* 0.6 and 4.9); δ_C(62.9 MHz; $CDCl_3$) 32.27, 122.6, 132.8, 137.3, 149.6 and 158.9; *m*/*z* (EI) 169 (M^+ + 1, 3%), 168 (M^+, 39), 141 (7), 140 (13), 91 (79), 77 (25), 73 (24), 65 (28), 51 (53), 43 (85), 39 (100).

9-Benzylidene-9*H*-fluorene 14

A mixture of fluorene (41 g, 0.25 mol), KOH (20 g, 0.36 mol) and benzaldehyde (40 ml, 0.4 mol) in benzyl alcohol (200 ml) was heated at 95 °C for 1.5 h. The hot reaction mixture was poured into H_2O (2 l) and left overnight. The crystalline precipitate was collected by filtration and the crystals were washed with EtOH. Recrystallisation gave the *title compound* as colourless crystals (46.3 g, 73%), mp 76–78 °C (from ethanol) (lit.,[13] 74–76 °C) (Found; C, 94.2; H, 5.7. $C_{20}H_{14}$ requires C, 94.5; H, 5.5%); ν_{max}(KBr)/cm^{-1} 3062m, 3028s, 3009m, 1575w, 1512m, 1448s, 1226s, 1215s, 1204m, 952m, 752s and 681m; δ_H(250 MHz; $CDCl_3$) 7.05–7.11 (1 H, m), 7.30–7.52 (6 H, m), 7.57–7.63 (3 H, m) and 7.72–7.82 (4 H, m); δ_C(62.9 MHz; $CDCl_3$) 119.8, 119.9, 120.5, 124.6, 126.8, 127.2, 127.5, 128.2, 128.4, 128.7, 129.5, 136.6, 136.7, 137.1, 139.4, 139.7 and 141.4 (one overlapping resonance); *m*/*z* (EI) 255 (M^+ + 1, 6%), 254 (M^+, 30), 253 (28), 252 (15), 91 (35), 78 (11), 77 (15), 73 (18), 57 (29), 55 (32), 51 (52), 43 (100).

2,7-Dibromo-9-(1-phenylmethylene)-9*H*-fluorene 15

A mixture of 2,7-dibromofluorene (3.0 g, 9.3 mmol) and KOH (1.04 g, 18.5 mmol) in EtOH (100 ml) was heated under reflux. A solution of benzaldehyde (1.08 g, 10.2 mmol) in EtOH (10 ml) was added to the reaction mixture and heating was continued for 0.5 h. The reaction mixture was left to cool to room temperature and the resulting solid was collected by filtration to yield the *title compound* (3.17 g, 83%) as pale yellow needles, mp 102–103 °C (from acetic acid) (lit.,[14] 98–99 °C) (Found: C, 58.2; H, 2.9. $C_{20}H_{12}Br_2$ requires C, 58.2; H, 3.0%); ν_{max}(KBr)/cm^{-1} 3059m, 2947m, 1619m, 1586m, 1442s, 1365m, 1275m, 1139m, 1070m, 943s, 810s, 778vs, 693s and 622m; δ_H(250 MHz; $CDCl_3$) 7.39–7.56 (9 H, m), 7.67 (2 H, s) and 7.86 (1 H, d, *J* 0.9); δ_C(62.9 MHz; $CDCl_3$) 120.8, 120.9, 121.0, 121.2, 123.7, 127.4, 128.8, 128.9, 129.2, 130.0, 131.2, 131.5, 134.5, 135.7, 137.0, 138.0, 139.1 and 141.7; *m*/*z* (EI) 410/412/414 (M^+, 42, 73, 44%), 332/334 (M^+ − Br, 8, 9), 252 (M^+ − 2Br, 3), 102 (96), 86 (100).

2,7-Dibromo-9-(2,5-dimethylphenylmethylene)-9*H*-fluorene 16

The same procedure as described above for **15** was followed, using 2,7-dibromofluorene (8.0 g, 25 mmol), 2,5-dimethylbenzaldehyde (3.3 g, 25 mmol) and KOH (6.9 g, 123 mmol) to yield the *title compound* (9.05 g, 83%) as yellow prisms, mp 134–136 °C (from acetic acid) (Found: C, 60.1; H, 3.6; Br, 36.4. $C_{22}H_{16}Br_2$ requires C, 60.0; H, 3.6; Br, 36.4%); ν_{max}(KBr)/cm^{-1} 3037w, 3017w, 2934w, 2915w, 1629m, 1599w, 1570w, 1494m, 1447s, 1427s, 1399m, 1374w, 1253m, 1064m, 880s, 801s, 741w, 687m and 632m; δ_H(250 MHz; $CDCl_3$) 2.29 (3 H, s), 2.36 (3 H, s), 7.14–7.21 (2 H, m), 7.24–7.28 (2 H, m), 7.36–7.39 (2 H, m), 7.40–7.57 (2 H, m), 7.67 (1 H, m) and 7.91 (1 H, d, *J* 1.2); δ_C(62.9 MHz; $CDCl_3$) 19.61, 20.89, 120.9, 121.0, 121.2, 123.7, 127.7, 129.7, 130.4, 131.1, 131.3, 133.6, 134.6, 134.7, 135.5, 137.1, 138.4, 138.9 and 140.9 (3 resonances are overlapping); *m*/*z* (EI) 439/441/443 (M^+, 48, 100, 49%), 363 (M^+ − Br, 20, 18), (M^+ − 2Br, 48), 266 (7), 179 (3), 153 (4), 143 (9).

9-Bromo-9-[bromo(phenyl)methyl]-9*H*-fluorene 17

9-Benzylidene-9*H*-fluorene **14** (12.5 g, 49 mmol) was suspended in HOAc (200 ml) and Br_2 (7.6 g, 48 mmol) was added dropwise with stirring. The reaction mixture was left at room temperature overnight and the precipitate collected by filtration and washed with Et_2O to give the *title compound* (18.4 g, 89%) as small colourless crystals, mp 113–115 °C (from ethanol) (lit.,[15] 112 °C) (Found: C, 58.3; H, 3.3. $C_{20}H_{14}Br_2$ requires C, 58.0; H, 3.4%); ν_{max}(KBr)/cm^{-1} 3059m, 3028m, 2961w, 1149m, 1605m, 1580m, 1447s, 1294m, 1211s, 1152s, 1075m, 1031m, 875s and 800m; δ_H(250 MHz; $CDCl_3$) 5.81 (1 H, s), 6.94–7.01 (4 H, m), 7.03–7.13 (1 H, m), 7.23–7.31 (2 H, m), 7.37–7.47 (3 H, m), 7.50–7.60 (2 H, m) and 8.07–8.12 (1 H, m); δ_C(62.9 MHz; $CDCl_3$) 62.20, 66.32, 120.0, 120.1, 126.0, 126.6, 127.3, 127.7, 127.9, 128.5, 129.5, 129.8, 136.5, 139.0, 139.5, 145.0 and 145.5 (one resonance is overlapping); *m*/*z* (EI) 412/414/416 (M^+, 5, 5, 5%), 335/333 (M^+ − HBr, 2, 2), 334/332 (M^+ − Br, 3, 3), 301 (22), 265 (10), 254 (M^+ − 2Br, 100).

2,7,9-Tribromo-9-[bromo(phenyl)methyl]-9*H*-fluorene 18

The same procedure as described above for **17** was followed, using **15** (6.4 g, 15.5 mmol) and Br_2 (2.5 g, 15.5 mmol) to yield the *title compound* (7.6 g, 85%) as colourless crystals, mp 176–178 °C (from ethanol) (Found: C, 42.1; H, 2.1. $C_{20}H_{12}Br_4$ requires C, 42.0; H, 2.1%); ν_{max}(KBr)/cm^{-1} 3041w, 3025w, 2957w, 1596w, 1571m, 1440s, 1417s, 1396m, 1245m, 1157s, 1062s, 940s, 845m, 805s, 778s, 763s, 724s, 698s and 643s; δ_H(250 MHz; $CDCl_3$) 5.64 (1 H, s), 7.01–7.19 (5 H, m), 7.25–7.44 (3 H, m), 7.53–7.57 (1 H, m), 7.64 (1 H, d, *J* 1.5) and 8.08 (1 H, d, *J* 1.8); δ_C(62.9 MHz; $CDCl_3$) 60.84, 64.31, 121.1, 121.2, 121.6, 127.5, 128.9, 129.7, 132.8, 133.0, 135.9, 137.1, 137.4, 146.8 and 147.5 (3 resonances are overlapping); *m*/*z* (EI) 568/570/572/574/576 (M^+, 2, 3, 7, 4, 2%), 488/490/492/494 (M^+ − Br, 8, 20, 23, 7), 459 (7), 410/412/414 (M^+ − 2Br, 52, 100, 54), 332/334 (M^+ − 3Br, 7, 10), 295 (2), 252 (M^+ − 4Br, 20).

2,7,9-Tribromo-9-[bromo-(2,5-dimethylphenyl)methyl]-9*H*-fluorene 19

The same procedure described for **17** was followed, using **16** (1.0 g, 2.3 mmol) and bromine (0.4 g, 2.3 mmol) to yield the *title compound* (0.94 g, 68%) as colourless crystals, mp 188–190 °C (from ethanol) (Found: C, 43.9; H, 2.6. $C_{22}H_{16}Br_4$ requires C, 44.0; H, 2.7%); ν_{max}(KBr)/cm^{-1} 3059w, 2919w, 1600w, 1573w, 1499w, 1450s, 1419m, 1399w, 1248w, 1159m, 1062m, 1006w, 946w, 892w, 813s, 739m, 685w and 647m; δ_H(250 MHz; $CDCl_3$) 2.17 (3 H, s), 2.19 (3 H, s), 5.77 (1 H, s), 6.87–6.99 (3 H, m), 7.35–7.48 (3 H, m), 7.54–7.58 (1 H, m), 7.73 (1 H, m) and 7.83 (1 H, d, *J* 1.5); δ_C(62.9 MHz; $CDCl_3$) 19.58, 21.03, 55.39, 65.03, 121.2, 121.3, 121.4, 122.0, 129.7, 129.9, 130.1, 130.5, 132.9, 133.0, 134.9, 135.2, 136.9, 137.4, 147.0 and 147.8 (2 resonances are overlapping); *m*/*z* (EI) 596/598/600/602/604 (M^+, 1, 1, 3, 1, 1%), 568 (3), 516/518/520/522 (M^+ − Br, 5, 11, 12, 4), 487 (12), 467 (7), 455 (33), 438/440/442 (M^+ − 2Br, 63, 100, 47), 427 (10), 411 (15), 383 (7), 374 (10), 358/360 (M^+ − 3Br, 13, 23), 280 (M^+ − 4Br, 27).

9-[Bromo(phenyl)methylene]-9*H*-fluorene 20

9-Bromo-9-[bromo(phenyl)methyl]-9*H*-fluorene **17** (18.4 g, 44 mmol) was suspended in HOAc (250 ml) and heated under reflux for 2 h. The reaction mixture was left to cool to room temperature overnight and the product was collected by filtration and dried under vacuum to give the *title compound* (11.3 g, 76%) as pale yellow crystals, mp 128–130 °C (from acetic acid) (lit.,[16] 127 °C) (Found C, 72.3; H, 4.0. $C_{20}H_{13}Br$ requires C, 72.1; H, 3.9%); ν_{max}(KBr)/cm^{-1} 3059m, 2947m, 1953w, 1918w, 1810w, 1619m, 1586m, 1442s, 1365m, 1275m, 1139m, 1070m, 943s, 810s, 778vs, 693s and 622m; δ_H(250 MHz; $CDCl_3$) 6.26 (1 H, d, *J* 7.9), 6.86–6.92 (1 H, m), 7.22–7.29 (1 H, m), 7.39–7.58 (7 H,

m), 7.65–7.69 (1 H, m), 7.71–7.77 (1 H, m) and 8.92 (1 H, m); δ_C(62.9 MHz; $CDCl_3$) 119.4, 119.6, 124.6, 124.8, 126.1, 126.9, 127.2, 128.2, 128.7, 129.2, 129.3, 136.2, 138.0, 138.3, 139.9, 141.3 and 142.9 (one resonance is overlapping); *m*/*z* (EI) 333/335 (M^+, 97, 100%), 255 ($M^+ - Br$, 48).

2,7-Dibromo-9-[bromo(phenyl)methylene]-9*H*-fluorene 21

The same procedure as described above for **20** was followed, using **18** (0.5 g, 1.2 mmol) to yield the *title compound* (0.4 g, 69%) as pale yellow crystals, mp 148–150 °C (from acetic acid) (Found: C, 48.9; H, 2.2. $C_{20}H_{11}Br_3$ requires C, 48.9; H, 2.2%); ν_{max}(KBr)/cm^{-1} 3067w, 1614m, 1587m, 1563m, 1442s, 1397s, 1228m, 1069s, 965s, 816s, 808s, 739s, 699s, 668s, 649w and 634w; δ_H(250 MHz; $CDCl_3$) 6.20 (1 H, d, *J* 1.5), 7.31–7.35 (1 H, m), 7.37–7.45 (3 H, m), 7.49–7.58 (5 H, m) and 8.98 (1 H, d, *J* 0.9); δ_C(62.9 MHz; $CDCl_3$) 120.5, 120.8, 121.0, 121.3, 127.7, 128.1, 128.3, 129.0, 129.2, 129.5, 129.9, 132.1, 134.4, 137.5, 139.0, 139.3, 139.5 and 141.9; *m*/*z* (EI) 488/490/492/494 (M^+, 33, 93, 100, 40%), 411/413/415 ($M^+ - Br$, 8, 21, 8), 331/333 ($M^+ - 2Br$, 8, 7), 253 ($M^+ - 3Br$, 2).

2,7-Dibromo-9-[bromo-(2,5-dimethylphenyl)methylene]-9*H*-fluorene 22

The same procedure as described above for **20** was followed, using **19** (0.46 g, 0.8 mmol) to yield the *title compound* (0.33 g, 82%) as pale yellow crystals, mp 230–232 °C (from acetic acid) (Found: C, 51.3; H, 2.9. $C_{22}H_{15}Br_3$ requires C, 50.9; H, 2.9%); ν_{max}(KBr)/cm^{-1} 3096w, 3059w, 2920w, 1619m, 1590m, 1565m, 1494m, 1446s, 1392m, 1261w, 1166w, 1069m, 968m, 810s, 754w and 669w; δ_H(250 MHz; $CDCl_3$) 2.22 (3 H, s), 2.37 (3 H, s), 6.13 (1 H, d, *J* 1.7), 7.09 (1 H, s), 7.17–7.28 (2 H, m), 7.33–7.37 (1 H, m), 7.43–7.47 (1 H, m), 7.50–7.60 (2 H, m) and 9.04 (1 H, m); δ_C(62.9 MHz; $CDCl_3$) 18.68, 21.01, 120.5, 120.8, 121.3, 121.4, 127.6, 127.9, 128.1, 129.1, 130.7, 131.1, 131.2, 131.8, 132.0, 134.4, 137.0, 137.4, 139.0, 139.1, 139.4 and 140.7; *m*/*z* (EI) 515/517/519/521 (M^+, 8, 13, 12, 4%), 437/439/441 ($M^+ - Br$, 14, 43, 42), 358/360 ($M^+ - 2Br$, 85, 88), 343/345 (27, 26), 280 ($M^+ - 3Br$, 100), 265 (48).

9-(9*H*-4,5-Diazafluoren-9-ylphenylmethylene)-9*H*-fluorene 23 (mixture of tautomers)

^{t}BuOK (0.33 g, 3.0 mmol) was added in portions to a stirred solution of **20** (0.82 g, 2.5 mmol) and 4,5-diazafluorene **12** (0.50 g, 3.2 mmol) in DMF (30 ml) under N_2. The reaction mixture was stirred overnight at room temperature. H_2O (150 ml) was then added and the reaction mixture neutralised with HOAc. The precipitate was collected by filtration and washed with water (10 ml). Chromatography on silica gel with petroleum ether 40–60 °C then ethyl acetate–ethanol (10 : 1) as eluent gave the *title compound* (0.45 g, 43%) as a dark violet solid, mp 148–151 °C; ν_{max}(KBr)/cm^{-1} 3057m, 2988m, 1676w, 1618w, 1596m, 1563m, 1446m, 1404s, 1167m and 703s; λ_{max}(EtOH)/nm 495sh (log ε 3.35), 480 (3.4), 332 (3.76); δ_H(400 MHz; $CDCl_3$) 5.20–5.62 (1 H, br s, exch. D_2O, NH), 5.88 (1 H, d, *J* 8.2), 6.08 (2 H, dd, *J* 8.2 and 1.0), 6.27 (2 H, s), 6.39 (1 H, s), 6.59 (6 H, t, *J* 7.9), 7.00–7.08 (3 H, m), 7.16–7.24 (8 H, m), 7.26–7.33 (8 H, m), 7.43 (2 H, t, *J* 7.2), 7.50 (4 H, d, *J* 7.5), 7.60 (4 H, d, *J* 7.5), 7.67 (2 H, d, *J* 7.5), 7.82 (1 H, d, *J* 7.5), 7.85 (2 H, d, *J* 7.5), 7.92 (1 H, dd, *J* 7.5 and 1.4), 8.28 (1 H, d, *J* 7.9), 8.50 (2 H, dd, *J* 4.8 and 1.0), 8.63–8.66 (4 H, m) and 8.72–8.75 (3 H, m); δ_C(100.6 MHz; $CDCl_3$) 49.4, 53.8, 120.3, 121.3, 123.5, 123.8, 123.9, 125.8, 125.9, 126.7, 126.8, 127.9, 128.2, 128.5, 128.9, 129.0, 129.0, 129.1, 129.4, 129.7, 130.3, 132.5, 132.9, 133.2, 134.1, 134.6, 134.7, 138.1, 138.5, 138.9, 139.2, 139.5, 139.9, 140.8, 142.6, 142.7, 143.0, 144.3, 150.4, 150.8, 150.9, 151.1, 156.2, 157.6, 159.1 and 160.1; δ_C (DEPT) 49.4, 53.8, 120.3, 121.3, 123.5, 123.8, 123.9, 125.8, 125.9, 126.7, 126.8, 127.9, 128.2, 128.5, 128.9, 128.95, 129.0, 129.1, 129.4, 129.7, 132.5, 132.9, 133.3, 134.7, 150.5, 150.9, 151.1 and 156.4; *m*/*z* (EI) 420.1621 (M^+. $C_{31}H_{20}N_2$ requires 420.1626), 421 ($M^+ + 1$, 13%), 420 (M^+, 48), 419 (21), 252 (17), 165 (29), 105 (46), 44 (100).

9-[(9*H*-4,5-Diazafluoren-9-yl)phenylmethylene]-9*H*-fluorene anion 23a

Typical procedure: to the precursor (35 mg) under an atmosphere of nitrogen was added DMSO-d_6 (1 ml). This was stirred and treated with ^{t}BuOK (2 equiv.) which resulted in the appearance of the dark blue colour of the anion. Sonication was used to promote solubilisation of the base. The solution was then filtered into an NMR tube and the spectrum recorded immediately. δ_H(250 MHz; DMSO-d_6) 6.30–6.62 (2 H, br s), 6.70 (2 H, dd, *J* 7.9 and 1.5), 6.72–6.79 (2 H, m), 6.82 (2 H, dd, *J* 7.9 and 4.3), 6.90–6.96 (2 H, m), 7.34–7.52 (5 H, m), 7.88 (2 H, d, *J* 7.3) and 8.18 (2 H, dd, *J* 4.3 and 1.5); δ_C (62.9 MHz; DMSO-d_6) 102.2, 114.1, 118.6, 118.8, 119.7, 121.4, 123.8, 126.3, 128.0, 128.2, 132.0, 132.2, 133.9, 139.1, 144.1, 144.5 and 147.5 (one resonance is overlapping).

2,7-Dibromo-9-[(9*H*-4,5-diazafluoren-9-ylidene)phenylmethyl]-9*H*-fluorene 24 (mixture of tautomers)

^{t}BuOK (0.62 g, 5.5 mmol) was added in portions to a stirred solution of **21** (1.22 g, 2.5 mmol) and 4,5-diazafluorene **12** (0.50 g, 3.2 mmol) in DMF (10 ml) and THF (30 ml) under N_2. The reaction mixture was stirred overnight at room temperature. H_2O (150 ml) was added and the reaction mixture neutralised with HOAc. The precipitate was collected by filtration and washed with H_2O (10 ml). Chromatography on silica gel with ethyl acetate–light petroleum (8 : 1) as eluent, followed by ethyl acetate yielded the *title compound* (0.64 g, 45%) as small dark violet crystals, mp decomp. >250 °C (Found: C, 64.3; H, 3.3; N, 4.9. $C_{31}H_{18}Br_2N_2$ requires C, 64.4; H, 3.1; N, 4.8%); ν_{max}(KBr)/cm^{-1} 3059w, 1655s, 1597w, 1439m, 1404s, 1385s, 1315m, 1278m, 1208m, 1184m, 1118m, 1062m, 1039m, 812m and 755m; λ_{max}(EtOH)/nm 534 (log ε 3.6), 288 (4.2); δ_H(400 MHz; $CDCl_3$) 1.76–2.12 (1 H, br s, exch. D_2O, NH), 5.82 (1 H, d, *J* 1.7), 6.08 (1 H, dd, *J* 8.2 and 1.0), 6.23 (1 H, s, exch. D_2O), 6.25 (1 H, s), 6.54 (2 H, d, *J* 7.2), 6.61 (2 H, d, *J* 7.2), 6.80 (1 H, dd, *J* 7.9 and 4.8), 7.00–7.07 (4 H, m), 7.10–7.14 (2 H, m), 7.24 (2 H, dd, *J* 7.9 and 4.8), 7.32 (1 H, dd, *J* 8.2 and 1.7), 7.36 (1 H, dd, *J* 7.9 and 4.8), 7.44 (4 H, s), 7.50 (1 H, dd, *J* 8.2 and 1.4), 7.62 (2 H, s), 7.67 (2 H, d, *J* 8.2), 7.86 (2 H, dd, *J* 7.5 and 1.0), 7.94 (2 H, dd, *J* 7.5 and 1.4), 8.38 (1 H, d, *J* 1.4), 8.51 (1 H, d, *J* 4.1), 8.56 (1 H, d, *J* 7.9), 8.66 (2 H, d, *J* 4.1) and 8.75 (1 H, dd, *J* 5.1 and 1.4); δ_C(100.6 MHz; $CDCl_3$) 49.3, 53.4, 121.4, 122.1, 122.3, 122.4, 122.5, 122.6, 123.6, 124.0, 124.1, 125.7, 128.7, 128.8, 129.1, 129.2, 129.4, 129.6, 129.9, 130.1, 130.3, 131.9, 132.2, 132.4, 132.5, 132.6, 132.7, 133.4, 133.4, 133.6, 134.3, 134.6, 137.9, 138.0, 138.5, 139.3, 140.7, 141.0, 146.1, 150.8, 151.2, 151.4, 156.2, 157.7 and 159.3; *m*/*z* (EI) 574.9758 ($M^+ - H$. $C_{31}H_{17}N_2Br_2$ requires 574.9761), 576/578/580 (M^+, 1, 2, 1%), 496/498 ($M^+ - Br$, 2, 2), 418 ($M^+ - 2Br$, 2), 348 (4), 323 (15), 307 (2), 293 (4), 271 (100), 257 (13), 183 (22), 168 (26), 105 (17).

2,7-Dibromo-9-[(9*H*-4,5-diazafluoren-9-yl)phenylmethylene]-9*H*-fluorene anion 24a

δ_H(250 MHz; DMSO-d_6) 6.47 (2 H, s), 6.74 (2 H, br s), 6.88–6.96 (2 H, m), 7.01 (2 H, d, *J* 7.9), 7.35–7.62 (5 H, m), 7.39 (2 H, d, *J* 7.9) and 8.27 (2 H, br s); δ_C(62.9 MHz; DMSO-d_6) 105.6, 109.6, 117.4, 119.7, 120.5, 120.8, 122.8, 127.3, 128.3, 128.8, 130.4, 131.8, 140.4, 141.2, 143.2, 145.8 and 149.4 (one resonance is overlapping).

9-[(9*H*-4,5-Diazafluoren-9-ylidene)-2,5-dimethyl]phenylmethyl)-2,7-dibromo-9*H*-fluorene 25 (mixture of tautomers)

^{t}BuOK (0.95 g, 8.5 mmol) was added portionwise to a stirred solution of **22** (2.00 g, 3.8 mmol) and 4,5-diazafluorene **12** (0.78

g, 5.1 mmol) in DMF (12 ml) and THF (36 ml) under N_2. The reaction mixture was stirred at room temperature overnight, diluted with CH_2Cl_2 (75 ml) and adsorbed onto silica gel. Chromatography on silica gel with diethyl ether followed by ethyl acetate–acetic acid (50 : 1) as eluent yielded the *title compound* (2.0 g, 87%) as small dark violet crystals, mp decomp. >250 °C (Found C, 65.1; H, 3.7; N, 4.5. $C_{33}H_{22}Br_2N_2$ requires C, 65.3; H, 3.6; N, 4.6%); ν_{max}(KBr)/cm^{-1} 3019s, 2980w, 1671m, 1405m, 1388m, 1224s, 1205s and 1167w; λ_{max}(EtOH)/nm 520 (log ε 3.6), 292 (4.48); δ_H(400 MHz; $CDCl_3$) 1.84 (s, Me), 1.91 (s, Me), 2.81 (s, Me), 2.88 (s, Me), 2.95–3.30 (1 H, br s, exch. D_2O, NH), 5.93 (1 H, s), 5.97 (1 H, d, *J* 1.4), 6.01 (1 H, s), 6.18 (1 H, s), 6.21 (1 H, s), 6.25 (1 H, dd, *J* 7.9 and 4.5), 6.74 (1 H, s), 6.81–6.85 (3 H, m), 7.09 (1 H, dd, *J* 7.9 and 4.5), 7.31–7.38 (3 H, m), 7.47 (2 H, s), 7.54 (1 H, s), 7.57 (1 H, s), 7.59 (1 H, s), 7.64 (1 H, d, *J* 7.9), 7.75 (1 H, d, *J* 7.9), 7.86 (1 H, d, *J* 7.9), 7.93 (1 H, s), 8.36 (1 H, d, *J* 1.3), 8.44 (1 H, br s), 8.53 (1 H, d, *J* 4.5), 8.57 (1 H, d, *J* 7.9), 8.66 (1 H, br s); δ_C(100.6 MHz; $CDCl_3$) 20.5, 21.8, 32.4, 37.5, 49.7, 53.7, 121.4, 121.9, 122.3, 122.3, 122.4, 122.5, 122.6, 123.6, 124.1, 124.2, 124.2, 127.7, 128.2, 129.0, 129.3, 129.8, 129.9, 130.1, 130.2, 130.4, 131.4, 131.6, 131.9, 132.1, 132.2, 132.5, 132.5, 132.6, 132.9, 132.9, 133.0, 134.3, 134.5, 134.7, 136.1, 136.4, 136.7, 137.2, 137.5, 138.4, 139.3, 139.4, 140.3, 140.5, 140.5, 141.3, 142.0, 145.5, 146.0, 146.2, 148.0, 150.7, 151.0, 151.1, 151.4, 157.5, 159.1, 159.6, 160.2 and 163.5; *m*/*z* (EI) 604.0150 (M^+. $C_{33}H_{22}N_2Br_2$ requires 604.0143) 603/605/607 (M^+, 37, 100, 47%), 577 (46), 525/527 (M^+ − Br, 5, 7), 445 (M^+ − 2Br, 4), 429 (7), 317 (16), 301 (22), 283 (49), 197 (16), 183 (100), 168 (11), 133 (58).

9-[(9*H*-4,5-Diazafluoren-9-yl)-2,5-dimethylphenylmethylene]-2,7-dibromo-9*H*-fluorene anion 25a

δ_H(250 MHz; DMSO-d_6) 1.72 (3 H, s), 2.25 (3 H, s), 6.57 (2 H, br s), 6.94 (2 H, br s), 7.01–7.38 (6 H, m), 7.79–8.01 (3 H, m) and 8.28 (2 H, br s); δ_C(62.9 MHz; DMSO-d_6) 18.9, 20.5, 105.5, 109.5, 117.6, 119.8, 120.4, 120.8, 122.5, 127.0, 129.0, 130.1, 130.3, 131.6, 134.4, 134.8, 141.1, 142.7, 145.0 and 149.4 (two resonances are overlapping).

Free radicals 26–28

Typical procedure.

9-[(9*H*-4,5-Diazafluoren-9-ylidene)phenylmethyl]-9*H*-fluoren-9-yl radical 26. ^{t}BuOK (53 mg, 0.47 mmol) was added to a stirred solution of compound **23** (199 mg, 0.47 mmol) in DMF (20 ml) under N_2 at room temperature which resulted in a colour change from purple to dark blue. A solution of $K_3Fe(CN)_6$ (156 mg, 0.47 mmol) in H_2O (8 ml) was added over 15 min and the brown solution stirred for a further 1 h. H_2O (100 ml) was added which precipitated a brown solid which was collected by filtration. The brown solid was dried under high vacuum to give the *title compound* (175 mg, 88%) as a brown solid, mp 138–140 °C; ν_{max}(KBr)/cm^{-1} 3062w, 3020m, 3000m, 1598m, 1563m, 1444m, 1402s, 1230s, 1220s, 1165m, 714m, 690s, 672s and 661s; λ_{max}(CH_2Cl_2)/nm 486 (log ε 2.9), 395 (3.4), 312 (2.0), 302 (2.3); EPR g = 2.0023, line width = 6.53 G; *m*/*z* (EI) 420 (M^+ + 1, 9%), 419 (M^+, 8), 357 (13), 272 (10), 270 (35), 252 (13), 241 (12), 183 (39), 180 (100), 165 (65), 152 (42), 105 (90), 77 (45).

2,7-Dibromo-9-[(9*H*-4,5-diazafluoren-9-ylidene)phenylmethyl]-9*H*-fluoren-9-yl radical 27. Yield 43%, brown solid, mp decomp. >250 °C; ν_{max}(KBr)/cm^{-1} 3060w, 1655s, 1637m, 1596m, 1561m, 1448s, 1402s, 1320w, 1269m, 1244m, 1182m, 1167m, 1118m, 1073m, 812m, 782w, 753w and 704w; λ_{max}(EtOH)/nm 477 (log ε 3.0), 303 (3.89), 291 (3.93); EPR g = 2.0023, line width = 6.71 G; *m*/*z* (CI) 593/594/595/596/597/598/599 (M^+ + NH_4, 50, 20, 100, 25, 60, 20, 3%).

9-[(9*H*-4,5-Diazafluoren-9-ylidene)-2,5-dimethylphenylmethyl]-2,7-dibromo-9*H*-fluoren-9-yl-radical 28. Yield 43%, brown solid, mp decomp. >250 °C (Found: C, 62.0; H, 3.6; N, 4.1. $C_{33}H_{21}Br_2N_2$·0.75H_2O requires C, 62.2; H, 3.8; N, 4.4%); ν_{max}(KBr)/cm^{-1} 3684w, 3025s, 2431w, 2400m, 1223s, 1206s, 791s, 674m; λ_{max}(EtOH)/nm 471 (log ε 3.4), 303 (4.4), 294 (4.4); EPR g = 2.0026, line width = 6.34 G; *m*/*z* (ESI) 647/645/643 (M^+ + K, 52, 100, 55%), 322 (16), 279 (24), 205 (25).

(9*H*-4,5-Diazafluoren-9-ylidene)phenylmethane 29

4,5-Diazafluorene **12** (100 mg, 0.60 mmol), KOH (120 mg, 0.21 mmol) and benzaldehyde (95 mg, 0.89 mmol) were dissolved in benzyl alcohol (2 ml) and heated at 40 °C for 2 d. H_2O (75 ml) was added and the mixture was extracted with CH_2Cl_2 (3 × 50 ml) and the combined organic extracts were dried over Na_2SO_4. Chromatography on silica gel with ethyl acetate as eluent gave the *title compound* (123 mg, 81%) as colourless crystals, mp 140–142 °C (from methanol–water 98 : 2) (Found: C, 81.7; H, 4.8; N, 10.9. $C_{18}H_{12}N_2$·0.5H_2O requires C, 81.5; H, 4.9; N, 10.6%); ν_{max}(KBr)/cm^{-1} 3099w, 3027m, 1643m, 1585m, 1558s, 1396s, 1344m, 1170s, 1072m, 815s, 750s, 719s and 700s; δ_H(250 MHz; $CDCl_3$) 7.07 (1 H, dd, *J* 4.9 and 7.9), 7.33 (1 H, dd, *J* 4.9 and 7.9), 7.39–7.58 (5 H, m), 7.79 (1 H, s), 7.84 (1 H, dd, *J* 1.2 and 7.9), 8.09 (1 H, dd, *J* 1.2 and 7.9), 8.64 (1 H, dd, *J* 1.2 and 4.9) and 8.72 (1 H, dd, *J* 1.2 and 4.9); δ_C(62.9 MHz; $CDCl_3$) 122.4 122.9, 127.6, 128.7, 128.8, 128.9, 129.3, 130.9, 131.2, 131.3, 131.4 133.8, 135.7, 150.4, 156.4 and 158.2; *m*/*z* (EI) 257 (M^+ + 1, 100%), 256 (M^+, 12).

(9*H*-4,5-Diazafluoren-9-ylidene)-2,5-dimethylphenylmethane 30

4,5-Diazafluorene **12** (0.5 g, 3.0 mmol), KOH (0.6 g, 10.8 mmol) and 2,5-dimethylbenzaldehyde (0.6 g, 4.5 mmol) were dissolved in benzyl alcohol (6 ml) and heated at 40 °C for 2 d. H_2O (175 ml) was added and the reaction mixture was extracted with CH_2Cl_2 (3 × 50 ml) and the combined organic extracts were dried over Na_2SO_4. Chromatography on silica gel with ethyl acetate–diethyl ether (1 : 1) as eluent yielded the *title compound* (0.81g, 95%) as colourless crystals, mp 93–95 °C (from methanol–water 98 : 2) (Found: C, 83.5; H, 5.7; N, 9.7. $C_{20}H_{16}N_2$·0.25H_2O requires C, 84.5; H, 5.6; N, 9.9%); ν_{max}(KBr)/cm^{-1} 3011w, 2917w, 1645m, 1586m, 1559s, 1494m, 1397s, 1340m, 1171s, 840s, 808s, 751s and 723m; δ_H(250 MHz; $CDCl_3$) 2.27 (3 H, s), 2.34 (3 H, s), 7.03 (1 H, dd, *J* 4.9 and 7.9), 7.09–7.25 (3 H, m), 7.32 (1 H, dd, *J* 4.9 and 7.9), 7.48 (1 H, dd, *J* 1.2 and 7.9), 8.11 (1 H, dd, *J* 1.2 and 7.9), 7.76 (1 H, s), 8.61 (1 H, dd, *J* 1.2 and 4.9) and 8.71 (1 H, dd, *J* 1.2 and 4.9); δ_C(62.9 MHz; $CDCl_3$) 19.60, 20.93, 122.6, 122.9, 127.7, 128.8, 129.3, 129.7, 130.4, 130.9, 131.1, 131.4, 131.6, 133.5, 133.6, 134.9, 135.5, 150.3, 156.5 and 158.0; *m*/*z* (EI) 285 (M^+ + 1, 21%), 284 (M^+, 100), 283 (72), 282 (13), 269 (35), 268 (37), 256 (13), 183 (52), 134 (23), 120 (22), 119 (47).

9-[(9*H*-4,5-Diazafluoren-9-ylidene)phenylmethyl]-9*H*-4,5-diazafluorene 31 (mixture of tautomers)

From **29**, yield 20%, as a dark purple solid, mp decomp. >250 °C; λ_{max}(EtOH)/nm 533, 308; ν_{max}(KBr)/cm^{-1} 3003s, 2963s, 2932m, 2860w, 2873w, 1598s, 1562s, 1468m, 1403s, 1385m, 1264s, 1228m, 1200s, 1165m, 1014w, 909s and 786m; δ_H(400 MHz; $CDCl_3$) 6.08 (1 H, dd, *J* 8.2 and 1.4), 6.22 (1 H, s), 6.51 (1 H, d, *J* 7.2), 6.56 (1 H, d, *J* 7.2), 6.78 (1 H, dd, *J* 8.2 and 4.8), 6.91–7.04 (4 H, m), 7.22 (1 H, dd, *J* 7.5 and 4.8), 7.34 (1 H, dd, *J* 8.2 and 4.8), 7.83 (1 H, d, *J* 7.5), 8.09 (1 H, dd, *J* 7.5 and 1.0), 8.43 (1 H, dd, *J* 4.8 and 1.4), 8.49 (1 H, dd, *J* 4.8 and 1.4), 8.58 (1 H, d, *J* 7.5), 8.64 (1 H, dd, *J* 4.8 and 1.0), 8.75 (1 H, dd, *J* 4.8 and 1.0), 3.81–4.84 (1 H, br s, exch. D_2O, NH), 5.58 (1 H, dd, *J* 8.2 and 1.4), 6.51 (1 H, d, *J* 7.2), 6.60 (1 H, dd, *J* 8.2 and 4.8), 7.05–7.12 (4 H, m), 7.22 (2 H, dd, *J* 7.5 and 4.8), 7.47 (1 H, dd, *J* 5.8 and 3.4), 7.65 (1 H, dd, *J* 5.8 and 3.4), 7.83, (2 H, d, *J* 7.5), 8.35 (1 H, dd, *J* 4.8 and 1.4), 8.56 (1 H, dd, *J* 4.4 and 1.0) and 8.64 (2 H, dd, *J* 4.8 and 1.0); δ_C(100.6 MHz; $CDCl_3$) 47.0, 123.6,

123.9, 124.0, 128.7, 129.3, 129.5, 129.5, 129.8, 129.9, 131.9, 132.7, 132.8, 133.4, 133.6, 134.2, 134.5, 134.6, 134.6, 137.8, 139.1, 147.4, 150.9, 151.3, 151.4, 151.5, 151.8, 151.9 and 160; *m*/*z* (EI) 422.1522 (M^+. $C_{29}H_{18}N_4$ requires 422.1531) 422 (M^+, 8%), 272 (12), 211 (17), 168 (100).

9-[(9*H*-4,5-Diazafluoren-9-ylidene)phenylmethyl]-9*H*-4,5-diazafluorene anion 31a

δ_H(250 MHz; DMSO-d_6) 6.69 (4 H, d, *J* 8.2), 6.88 (4 H, dd, *J* 8.2 and 4.6), 7.35–7.55 (5 H, m) and 8.25 (4 H, dd, *J* 4.6 and 0.9); δ_C(62.9 MHz; DMSO-d_6) 105.0, 119.5, 126.9, 128.3, 128.8, 131.8, 132.8, 140.9, 143.2, 146.2 and 149.2.

9-[(9*H*-4,5-Diazafluoren-9-ylidene)-2,5-dimethylphenylmethyl]-9*H*-4,5-diazafluorene 32 (mixture of tautomers)

Typical procedure: ^{t}BuOK (142 mg, 1.3 mmol) was added in portions to a solution of diazafluorene **12** (213 mg, 1.3 mmol) and (9*H*-4,5-diazafluoren-9-ylidene)-2,5-dimethylphenylmethane **30** (300 mg, 1.38 mmol) in DMF (14 ml) under N_2. After 3 h at room temperature, air was bubbled into the reaction mixture for 1 h. H_2O (30 ml) was added and the reaction mixture neutralised with HOAc. The precipitate was collected by filtration and washed with H_2O (10 ml). Chromatography on silica gel with ethyl acetate, ethyl acetate–ethanol (1:1) and ethyl acetate–ethanol–ammonia (10:10:1) as the eluents gave the *title compound* (96 mg, 20%) as a dark purple solid, mp decomp. >250 °C; ν_{max}(KBr)/cm^{-1} 3442s, 3062w, 2924w, 1653s, 1641s, 1564m, 1463s, 1383s, 1316m, 1262m, 1198s, 1163s, 1103m, 1026m, 809w, 753w, 702w and 657w; λ_{max}(EtOH)/nm 575 (log ε 4.23), 545sh (4.23), 442 (3.75), 296 (4.47); δ_H(400 MHz; $CDCl_3$) 1.87 (3 H, s), 1.90 (3 H, s), 5.99 (1 H, s), 6.23 (1 H, s), 6.24 (1 H, dd, *J* 7.9 and 1.4), 6.81–6.87 (3 H, m), 7.12 (1 H, dd, *J* 7.5 and 4.8), 7.25 (1 H, dd, *J* 7.9 and 4.8), 7.36 (1 H, dd, *J* 7.9 and 4.8), 7.74 (1 H, d, *J* 7.5), 7.83 (1 H, d, *J* 7.9), 8.54 (1 H, dd, *J* 4.8 and 1.4), 8.58–8.61 (2 H, m), 8.74 (1 H, d, *J* 4.8) and 8.77 (1 H, dd, *J* 4.8 and 1.4); δ_C(100.6 MHz; $CDCl_3$) 20.7, 21.7, 49.7, 123.6, 124.0, 124.1, 127.7, 129.8, 130.5, 131.6, 131.9, 132.1, 132.8, 132.9, 133.4, 134.2, 134.2, 134.6, 136.8, 137.4, 139.1, 139.2, 147.0, 151.0, 151.2, 151.3, 151.6, 157.6, 159.3, 159.7 and 160.2; *m*/*z* (EI) 449.1766 (M^+ − H. $C_{31}H_{22}N_4$ requires 449.1774) 451 (M^+ + 1, 61%), 423 (100).

9-[(9*H*-4,5-Diazafluoren-9-ylidene)-2,5-dimethylphenylmethyl]-9*H*-4,5-diazafluorene anion 32a

δ_H(250 MHz; DMSO-d_6) 1.71 (3 H, s), 2.24 (3 H, s), 6.65–6.85 (4 H, br s), 6.87 –6.96 (4 H, m), 7.10 (1 H, s), 7.17 (1 H, d, *J* 7.9), 7.25 (1 H, m) and 8.25 (4 H, d, *J* 3.4); δ_C(62.9 MHz; DMSO-d_6) 18.8, 20.5, 105.0, 119.8, 126.7, 129.1, 130.2, 131.7, 134.4, 134.8, 140.9, 142.8, 145.5 and 149.1 (one overlapping resonance).

9-[(9*H*-4,5-Diazafluoren-9-ylidene)phenylmethyl]-9*H*-4,5-diazafluoren-9-yl radical 33

^{t}BuOK (14 mg, 0.12 mmol) was added to a stirred solution of **32** (52 mg, 0.12 mmol) in EtOH (10 ml) under nitrogen at room temperature resulting in a colour change from purple to dark blue. A solution of $K_3Fe(CN)_6$ (41 mg, 0.12 mmol) in water (3 ml) was added. Water (20 ml) was added and the solution was extracted with toluene (3 × 15 ml). The combined organic extracts were dried over sodium sulfate and the solvent removed under reduced pressure to give the *title compound* as a brown powder (40 mg, 77%), mp >250 °C; EPR g = 2.0025, line width = 6.71 G; ν_{max}($CHCl_3$)/cm^{-1} 3055w, 1562s, 1442w, 1401s, 1344w, 1261m, 1163m, 1097m, 1075w, 812m, 751s, 730m and 704m; λ_{max}($CHCl_3$)/nm 458 (log ε 4), 312sh (4.3), 294 (4.4); *m*/*z* (EI) 444 (M^+ + Na, 17%), 423 (M^+ + 2, 100), 422 (M^+ + 1, 9), 205 (8), 96 (52).

9-[(9*H*-4,5-Diazafluoren-9-ylidene)-2,5-dimethylphenylmethyl]-9*H*-4,5-diazafluoren-9-yl radical 34

^{t}BuOK (25 mg, 0.22 mmol) was added to a stirred solution of **31** (100 mg, 0.22 mmol) in DMF (25 ml) under nitrogen at room temperature, resulting in a colour change from purple to dark blue. A solution of potassium hexacyanoferrate(II) (73 mg, 0.22 mmol) in water (4 ml) was added over 10 min and the brown solution stirred for a further 1 h. Water (100 ml) was added and the solution extracted with toluene (3 × 30 ml). The combined organic extracts were dried over sodium sulfate and the solvent removed under reduced pressure to give the *title compound* as a brown powder (76 mg, 76%), mp >250 °C; EPR g = 2.0025, line width = 6.08 G; ν_{max}($CHCl_3$)/cm^{-1} 3058w, 1563s, 1467w, 1401s, 1342w, 1261s, 1198w, 1164m, 1097m, 1025m, 811m and 754s; λ_{max}($CHCl_3$)/nm 450 (log ε 3.6), 314 (4.1), 301 (4.1); *m*/*z* (ES) 472 (M^+ + Na, 37%), 451 (M^+ + 2, 19), 450 (M^+ + 1, 4), 205 (100), 183 (12), 102 (13).

9-[(9*H*-Fluoren-9-ylidene)phenylmethyl)-9*H*-fluorene 35

^{t}BuOK (4.5 g, 40 mmol) was added portionwise to a stirred solution of **14** (3.33 g, 10 mmol) and fluorene (1.82 g, 11 mmol) in DMF (60 ml) under an atmosphere of nitrogen. After 1 h at room temperature, hydrochloric acid (1.8 M, 50 ml) was added and the reaction mixture added to water (500 ml) to give an orange precipitate. This was collected by filtration, washed with water (30 ml) and methanol (30 ml) and dried under vacuum at 50 °C. The solid was recrystallised to give the *title compound* (3.3 g, 80%), as small pale yellow needles, mp 245–246 °C (from benzene) (lit.,[2] 235–236 °C); ν_{max}(KBr)/cm^{-1} 3056w, 3035w, 3011w, 1590w, 1473w, 1444s, 1349w, 1270w, 1027w, 844w, 782s, 760s, 741s, 704s, 645m and 619m; δ_H(400 MHz; $CDCl_3$) 5.87 (1 H, d, *J* 7.9), 6.46 (1 H, s), 6.62 (1 H, d, *J* 1.4), 6.64 (1 H, s), 6.76–6.80 (1 H, m), 6.96 (2 H, t, *J* 7.5), 7.02–7.06 (1 H, m), 7.17–7.24 (3 H, m), 7.28–7.35 (3 H, m), 7.43 (1 H, t, *J* 7.5), 7.56 (2 H, d, *J* 7.5), 7.62 (2 H, d, *J* 7.5), 7.71 (1 H, d, *J* 7.5), 7.85 (1 H, d, *J* 7.2) and 8.41 (1 H, d, *J* 8.2); δ_C(100.6 MHz; $CDCl_3$) 53.7, 120.1, 120.9, 121.0, 126.1, 126.5, 127.1, 127.6, 128.0, 128.2, 128.3, 128.4, 128.5, 128.8, 129.2, 129.4, 137.0, 139.6, 139.8, 140.0, 140.8, 142.4, 143.0, 145.2 and 146.2; *m*/*z* (EI) 418 (M^+, 100%).

9-[(9*H*-Fluoren-9-ylidene)phenylmethyl]-9*H*-fluorene anion 35a

δ_H(250 MHz; DMSO-d_6) 6.45 (4 H, d, *J* 7.9), 6.74 (4 H, td, *J* 7.9 and 1.2), 6.85 (4 H, td, *J* 7.3 and 1.2), 7.34–7.36 (3 H, m), 7.38–7.48 (2 H, m) and 7.89 (4 H, d, *J* 7.3); δ_C(62.9 MHz; DMSO-d_6) 110.9, 117.7, 118.3, 120.8, 123.0, 127.7, 132.2, 132.3, 139.0, 143.8 and 144.9 (one overlapping resonance).

9-[(9*H*-4,5-Diazafluoren-9-ylidene)phenylmethyl]-9*H*-fluoren-9-ylradical $CuCl_2$ complex

A solution of cupric chloride dihydrate (20 mg, 0.12 mmol) in ethanol (2 ml) was added to a solution of free radical **23a** (50 mg, 0.12 mmol) in dry ethanol (5 ml) under nitrogen. After stirring at room temperature for 30 min a brown precipitate was collected by filtration, washed with ethanol (3 × 5 ml) and dried under high vacuum to give a brown solid (30 mg, 45%) (Found: C, 68.4; H, 3.3; N, 4.9. $C_{62}H_{38}N_4Cu_2Cl_4$ requires C, 67.1; H, 3.4; N, 5.05%); ν_{max}(KBr)/cm^{-1} 3064w, 1625s, 1602s, 1578s, 1439m, 1410s, 1295m, 1236m, 1165m, 1041m, 1016m and 742s.

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