Extending conjugation in porphyrin dimer carbocations†

Karl J. Thorley and Harry L. Anderson*

The addition of alkynyl porphyrins to carbonyl compounds was used to prepare a series of porphyrin dimer tertiary alcohols. Treatment of these alcohols with acid gave conjugated carbocations with three to nine carbon atoms bridging between the porphyrins. All these carbocations show strong absorption in the near-IR region between 1000–1800 nm. The absorption spectra exhibit a length-dependence similar to that of polymethine cyanines, with a bathochromic shift of approximately 200 nm (900 cm^{-1}) per alkyne. The longest of these chromophores has an absorption maximum at 1623 nm (in CHCl$_3$ with 2% trifluoroacetic acid). The symmetry of the π-system has a strong effect on the position, intensity and width of the absorption bands. The stability of the cations in solution decreases with increasing bridge length.

Introduction

Nonlinear optical dyes operating in the near-IR spectral region (1000–2000 nm wavelength) have important potential applications for telecommunications.[1] These include all-optical signal processing devices such as optical switches,[2,3] optical correlators[4,5] and optical limiters.[6,7] Absorption of near-IR light is important for photodetectors used in applications such as thermal imaging and night vision. Dyes absorbing in the near-IR are needed for light harvesting applications.[8,9]

Near-IR dyes include cyanines, squaraines and phthalocyanines.[10,11] Dyes absorbing beyond 1000 nm are rare and include cationic porphyrinoids,[12] quinoidal structures[13,14] extended aromatic systems,[15–17] cyanines[18] and donor–acceptor systems.[19] The fused porphyrin tapes reported by Osuka exhibit the longest wavelength absorption bands of any organic dyes, which extend into the vibrational region of the infrared.[20]

We have previously reported the synthesis and properties of cationic porphyrin dimers, such as **1**$^+$, which we loosely referred to as "porpho-cyanines".[21] The conjugated bridge differs from that of traditional cyanines as it features ethynyl groups to increase electronic communication by avoiding steric repulsion.[22] Despite the large bond length alternation, these compounds show linear and nonlinear optical properties which are similar to those of cyanine dyes, but at longer wavelengths. The near-IR band of **1**$^+$ has an absorption maximum at 1243 nm, with an exctinction coefficient of 1.7×10^5 M^{-1} cm^{-1} (Fig. 1). The position of this absorption maximum is sensitive to changes in substituents on the central phenyl group; *para*-nitro or methoxy substituents result in shifts of around 100 nm.

Cyanines show a strong correlation between optical properties and molecular length, L,[1,23] with the polarisability α scaling as L^3 and the second hyperpolarisability γ scaling with L^7. Here
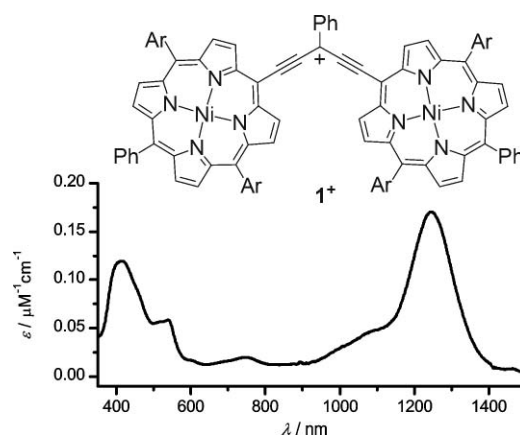
Fig. 1 Structure of cationic porphyrin dimer **1**$^+$ and the UV/Vis/NIR spectrum measured in CHCl$_3$/2% TFA at 298 K. Ar = 3,5-di-*t*-butyl phenyl.

we report an investigation of the relationship between the length of the bridge in extended analogues of porphyrin dimer cations such as **1**$^+$ and their optical properties. At the outset of this work, it was not clear whether extending the acetylenic link in cation **1**$^+$ would result in a fully conjugated system. Increasing the distance of the carbocation centre from the porphyrins might be expected to reduce the electronic coupling resulting in a blue-shifted absorption. However, we found that the extended systems have strongly red-shifted absorption spectra.
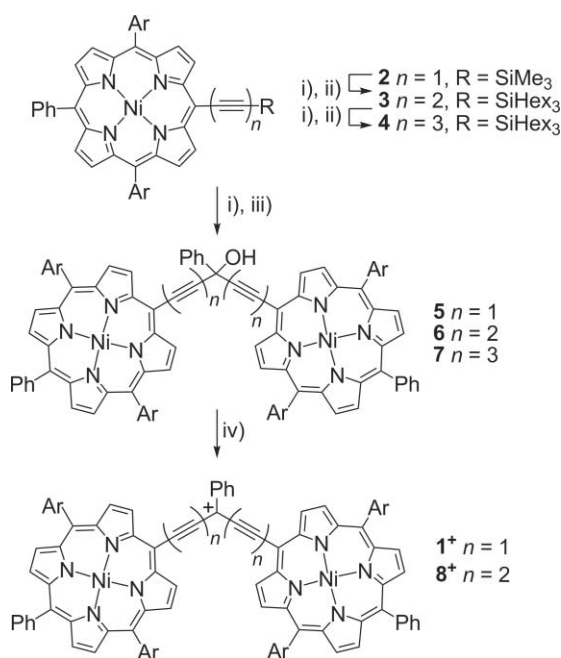
Results and discussion

Synthesis

The previously reported porpho-cyanine **1**$^+$ was prepared by addition of trifluoroacetic acid to porphyrin dimer alcohol **5**, which was synthesised by deprotonation of acetylenic porphyrin **2** and subsequent trapping with an aromatic ester (Scheme 1). Using a similar methodology, longer systems were synthesised. Butadiyne porphyrin monomer **3** was prepared by Glaser–Hay coupling of the acetylene porphyrin with an excess of trihexylsilylacetylene.[24,25]

Department of Chemistry, Chemistry Research Laboratory, University of Oxford, 12 Mansfield Road, Oxford, UK OX1 3TA. E-mail: harry.anderson@chem.ox.ac.uk; Fax: +44 1865 285002; Tel: +44 1865 275704

3472 | *Org. Biomol. Chem.*, 2010, **8**, 3472–3479

This journal is © The Royal Society of Chemistry 2010

Scheme 1 *Reagents and conditions*: i) Bu₄NF, CH₂Cl₂, 20 °C, quant. ii) HCCSiHex₃, CuCl, TMEDA, air, CH₂Cl₂, THF, 20 °C (**3**: 91%; **4**: 95%); iii) PhCO₂Me, LiN(SiMe₃)₂, THF, 20 °C (**5**: 53%; **6**: 31%; **7**: N/A); iv) CF₃CO₂H, CHCl₃.

Reaction of **3** with methyl benzoate gave the extended nine-carbon dimer **6** (Scheme 1). Addition of trifluoroacetic acid to a solution of **6** in CHCl₃ resulted in formation of cation **8⁺**.

Similarly, Glaser–Hay coupling between butadiyne monomer **3** and an excess of trihexylsilylacetylene gave the hexatriyne porphyrin **4**. Subsequent deprotection and reaction with methyl benzoate, gave the thirteen-carbon dimer **7**. This dimer proved to be fairly unstable during chromatography and could not be fully purified.

Another extended porphyrin dimer (**11**, Scheme 2) was synthesised with *para*-phenylene spacers in the bridge. The separation
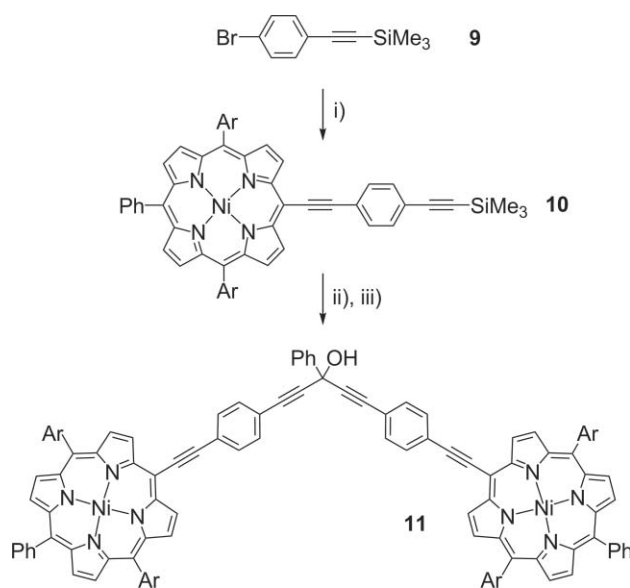
Scheme 2 *Reagents and conditions*; i) **2**, Pd₂(dba)₃, PPh₃, CuI, NEt₃, PhMe, 40 °C, 48%; ii) Bu₄NF, CH₂Cl₂, 20 °C, quant. iii) PhCO₂Me, LiN(SiMe₃)₂, THF, 20 °C, 14%.

of the successive alkyne groups was explored as an approach to increase the stability of the porphyrin dimer, both as the alcohol and eventually as the carbocation. The porphyrin monomer **10** was formed by a selective Sonogashira coupling reaction of 4-bromo-iodobenzene, before reaction to give dimer **11** under the conditions used for dimers **5–7**.

In addition to forming longer systems using the original methodology, it was possible to form dimers in a stepwise manner. This gave access to unsymmetrical porphyrin dimers. Formyl porphyrin **12** was prepared by Vilsmeier formylation.[26] Reaction of acetylene porphyrin **2** with the formyl porphyrin under basic conditions gave the three-carbon bridged dimer **13**. Similarly, a porphyrin dimer with five bridging carbons was formed by reaction of butadiyne porphyrin **3** with formyl porphyrin **12** (Scheme 3).
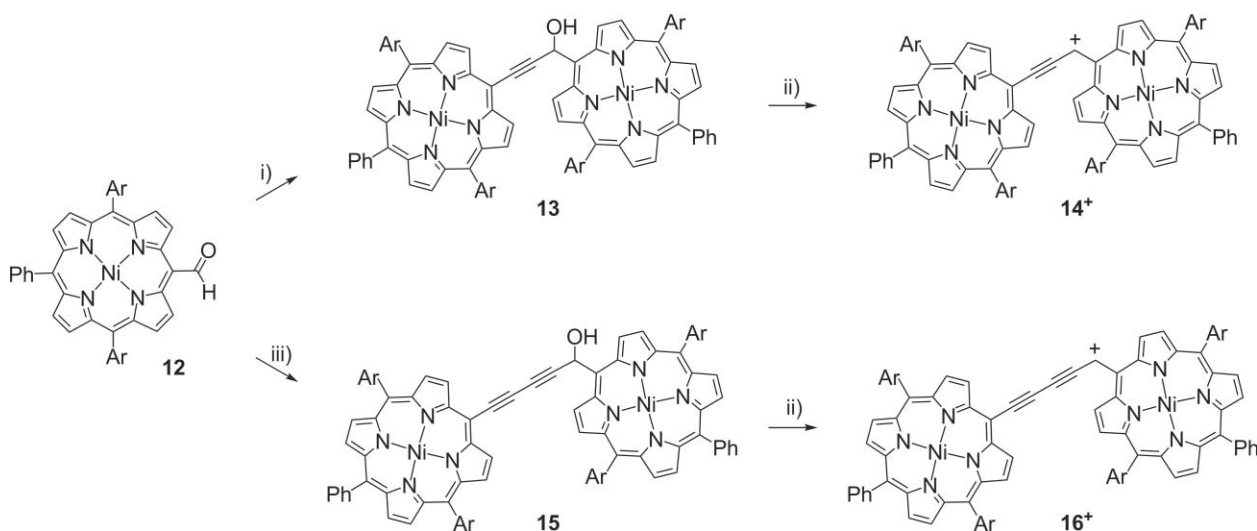
Scheme 3 *Reagents and conditions*: i) **2** (after silyl deprotection), LiN(SiMe₃)₂, THF, 20 °C, 30%; ii) CF₃CO₂H, CHCl₃; iii) **3** (after silyl deprotection), LiN(SiMe₃)₂, THF, 20 °C, 63%.

Finally for the synthesis of a seven-carbon dimer **18**, the intermediate ketone **17** was required. This was achieved by reacting the acetylene porphyrin with *N*-methyl-*N*-methoxy benzamide.[27] Reaction of the resulting ketone with the butadiyne porphyrin monomer **3** gave the seven-carbon dimer (Scheme 4).
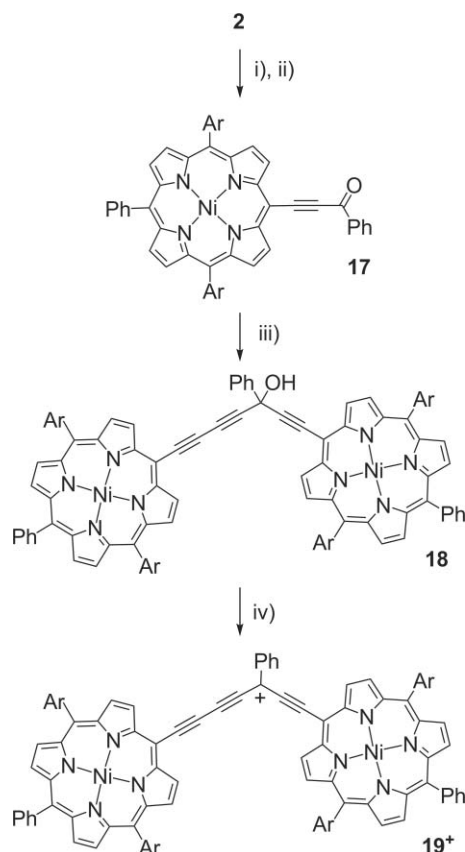

Scheme 4 *Reagents and conditions*: i) Bu$_4$NF, CH$_2$Cl$_2$, 20 °C, quant. ii) PhC(O)N(OMe)Me, LiN(SiMe$_3$)$_2$, THF, 20 °C, 83%; iii) **3** (after silyl deprotection), LiN(SiMe$_3$)$_2$, THF, 20 °C, 30%; iv) CF$_3$CO$_2$H, CHCl$_3$.

Absorption spectra

Addition of trifluoroacetic acid to the tertiary alcohols resulted in the formation of the corresponding cations (Table 1). UV/Vis/NIR spectroscopy was used as the primary technique for investigating the cations. Cationic porphyrin dimers **8**⁺, **14**⁺, **16**⁺

and **19**⁺ showed absorption bands in the near-IR, while addition of trifluoroacetic acid to extended dimers **7** (which contained some monomer impurities) and **11** did not result in any near-IR absorption. A reduction in intensity of the Soret band at 400 nm was observed, suggesting that the desired carbocations may be formed, but, if they are formed, they decompose before their near-IR absorption spectra can be observed.

The absorption spectra of the porphyrin carbocations are shown in Fig. 2. The increase in λ_{max} with bridge length is immediately obvious. There is an approximate 200 nm shift with each alkyne added. However, the unsymmetrical cationic dimers **14**⁺ and **19**⁺ show weaker and broader absorption bands than the symmetrical systems. Furthermore, the absorption maximum for the seven-carbon dimer **19**⁺ does not lie directly between those for the five- and nine-carbon dimers.
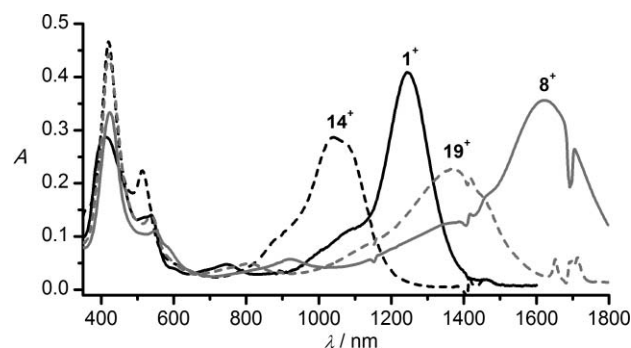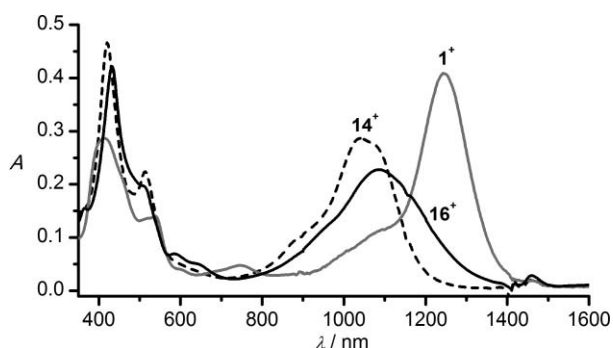

Fig. 2 Absorption spectra of cations **14**⁺ (C3, black dash), **1**⁺ (C5, black solid), **19**⁺ (C7, grey dash) and **8**⁺ (C9, grey solid) measured in CHCl$_3$/2% TFA at 298 K. Spectra are normalised to the Soret maxima of the parent alcohols.

It is interesting to compare the absorption spectra of the two C5 bridge compounds **16**⁺ and **1**⁺ (Fig. 3). The lower symmetry of **16**⁺ results in a substantially broader absorption band (FWHM = 2324 cm⁻¹, *vs.* 920 cm⁻¹ for **1**⁺). The higher symmetry of **1**⁺ also shifts the absorption to longer wavelength (1248 nm *vs.* 1087 nm for **16**⁺), although the central Ph group in **1**⁺ also contributes to this shift. The absorption spectrum of **16**⁺ is more similar to that of the C3 bridged cation **14**⁺ in position, but is again broader. This similarity can be accounted for by comparison of the structures of the two cations; the positive charge is formed adjacent to one of the porphyrins in both cases, with the second porphyrin located further away *via* an alkynyl bridge.

Table 1 NIR absorption properties of cations generated *in situ* from alcohols by addition of 2% TFA (by volume). Extinction coefficients are calculated assuming quantitative cation formation.[28]

Cation	Bridge ($x : y$)	R	λ_{max}/nm	ε/μM⁻¹cm⁻¹	FWHM/cm⁻¹
14⁺	0 : 1	H	1042	0.12	2175
16⁺	0 : 2	H	1087	0.095	2324
1⁺	1 : 1	Ph	1248	0.17	920
19⁺	1 : 2	Ph	1378	0.094	1634
8⁺	2 : 2	Ph	1623	0.16	1134

Fig. 3 Absorption spectrum of cations 14^+ (C3, black dash), 16^+ (unsymmetrical C5, black solid) and 1^+ (symmetrical C5, grey solid) measured in $CHCl_3$/2% TFA at 298 K.

The trend in absorption maximum can be summarised by plotting λ_{max} against the bridge length, N (number of carbons in the bridge). Theoretically, for true cyanine structures, as the polymethine chain becomes infinitely long, the wavelength of absorption tends to an infinite value. This trend is more obvious when plotting the frequency against the reciprocal bridge length, where the HOMO–LUMO gap tends toward zero as N^{-1} tends to zero.[1] Fig. 4 shows the data for the five porphyrin carbocations. A clear length dependence can be seen, with the shortest compounds having the highest energy absorption maxima. The lines join points of equal symmetry ($x = y$, $y + 1$ or $y + 2$). The gradients of these lines show that the most symmetrical dimers exhibit a stronger length dependence and lower energy transitions than the unsymmetrical dimers. The synthesis of additional porphyrin cations of differing length and symmetry is needed to fully explore this effect, although changing substituents and steric environments makes it difficult to directly compare different series.
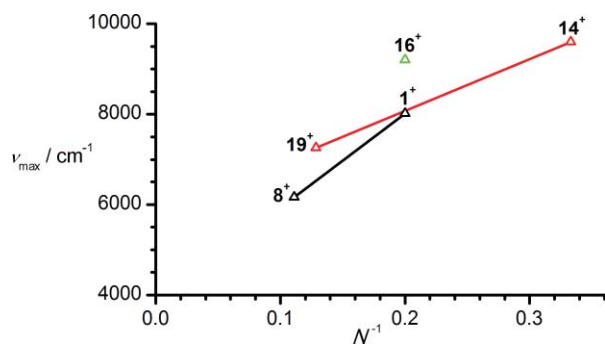
Fig. 4 Plot of v_{max} against N^{-1} where N is the number of carbon atoms in the alkyne bridge. The lines join compounds of similar symmetry *i.e.* $x = y$ (black), $x = y + 1$ (red) and $x = y + 2$ (green). v_{max} is the frequency of the peak of the absorption band, measured in $CHCl_3$/2% TFA.

Mass spectrometry

The mass spectra of the tertiary alcohols provide some insight into the stability of the carbocations (Fig. 5). In each case, two peaks were observed with a difference of 17 Da between the two peaks. The higher molecular weight peak was due to the alcohol $[ROH]^{\bullet+}$, while the lower molecular weight peak corresponded to the carbocation R^+ formed by protonation and loss of water. There are two competing ionisation processes. As the bridge length
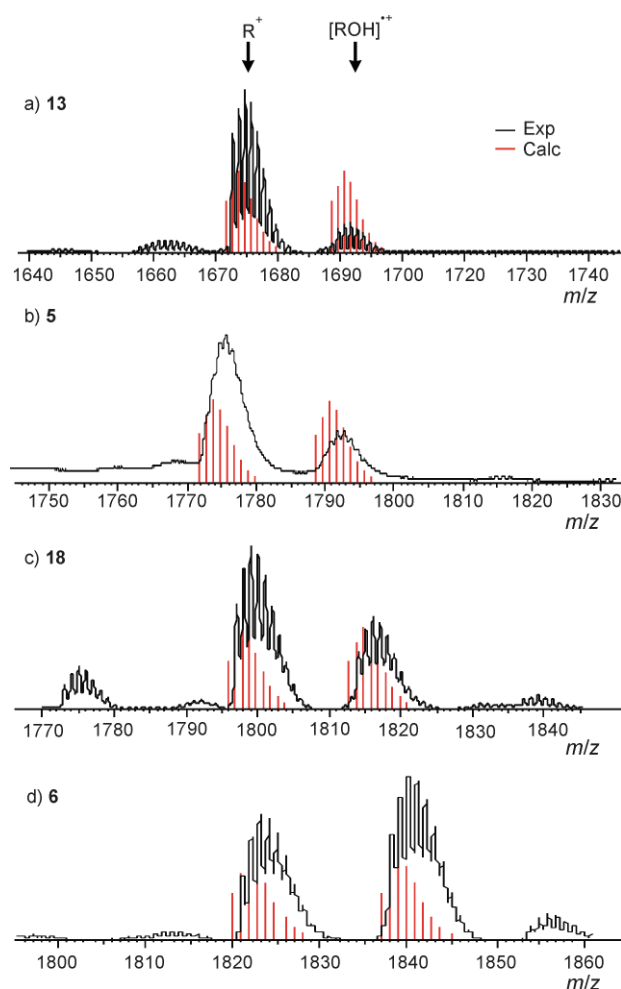
Fig. 5 MALDI-TOF spectra of porphyrin dimer alcohols ROH = **13**, **5**, **18** and **6** (a) to d) respectively). The red lines show the calculated isotopic patterns for the alcohol $[ROH]^{\bullet+}$ and cation formed by protonation and dehydration R^+ in each case. Dithranol was used as the matrix.

increases from **13** to **6**, the alcohol peak becomes more intense than the carbocation peak. Direct oxidation of the porphyrin π-system is more favourable in the longer systems, whereas protonation and dehydration is more favourable in the shorter systems.

Cation stability

Upon increasing the bridge length, there is a decrease in the stability of the carbocation, with the thirteen-carbon dimer **7** showing no detectable near-IR band upon addition of acid. To investigate this further, the absorption spectra of the cationic dimers were monitored over time. The five-carbon dimer 1^+ showed slow decomposition over a period of days to give an absorption spectrum consistent with a non-conjugated porphyrin, although not identical to the alcohol precursor.

In contrast, the absorption spectrum of the C9 dimer 8^+ changed rapidly, with a half life of 570 s at an acid concentration of 1% TFA (Fig. 6). At low acid concentrations, the band at 1623 nm was seen to decrease, while a new band appeared at 1250 nm (Fig. 7a). Other alkynyl bridged carbocations have previously been shown to react with water to give pyrylium ions.[29] The relative rates of reaction of 1^+ and 8^+ are consistent with this decomposition pathway, as
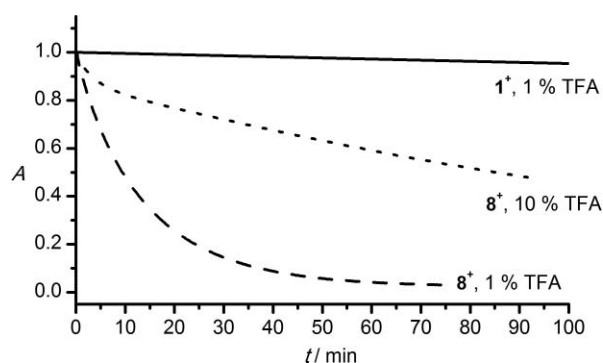
Fig. 6 Absorption at λ_{max} plotted against time for cation 1^+ measured in CHCl$_3$/1% TFA (solid line) and cation 8^+ measured in CHCl$_3$/1% TFA (dashed line) and in CHCl$_3$/10% TFA (dotted line).

the more sterically hindered bridge of the C5 dimer is the more stable. Formation of a pyrylium is also consistent with the observed changes in the NIR spectra, but the final products could not be identified due to the broadness of their NMR spectra.

At higher acid concentrations the additional near-IR band at 1250 nm is not observed, and the cation is more stable (Fig. 7b). At acid concentrations above 15% by volume the stability decreased. The stability of cation 8^+ at different acid concentrations was compared by plotting the absorption at λ_{max} over time (Fig. 7c). By plotting the absorption after an arbitrary time of 500 s against the acid concentration (Fig. 7d, bars), the optimum stability was found to be between 10 and 15% TFA by volume (1.3 M and 2.0 M). By fitting the data to exponential decay curves, the initial rates k_0

were also determined. Plotting $-k_0$ against the acid concentration gave the same optimum acid concentration (Fig. 7d, crosses).

Conclusions

A series of carbocation porphyrin dimers, based on the previously reported structure 1^+, were synthesised which varied by the length of the conjugated bridge between the porphyrin end groups. Delocalised carbocations with bridge lengths of three to nine carbon atoms were found to be stable enough for UV/Vis/NIR absorption measurements under ambient conditions. The absorption spectra of the series of stable carbocations show a shift of approximately 200 nm per alkyne, which is similar to the length dependence in cyanine dyes, despite large bond length alternation. The symmetry of the π-system is important to the position, intensity and width of the absorption bands.

Unfortunately, while increasing the bridge length gave large shifts in absorption, a reduction in stability was also observed. Attempts at synthesising a carbocation with thirteen carbon atoms in the bridge were unsuccessful; C9 appears to represent the limit of stability. This could be due to the decrease in steric bulk around the bridge, or due to the onset of a "cyanine limit" effect from a reduction in electronic coupling.[30] The stability of the five and nine-carbon bridged carbocations was found to be dependant on the acid concentration.

The longest near-IR band was observed for the C9 dimer 8^+, with λ_{max} of 1623 nm and an extinction coefficient of 160 000 M^{-1}cm^{-1}. This is among the longest wavelength electronic absorption bands observed for an organic π-system. The near-IR
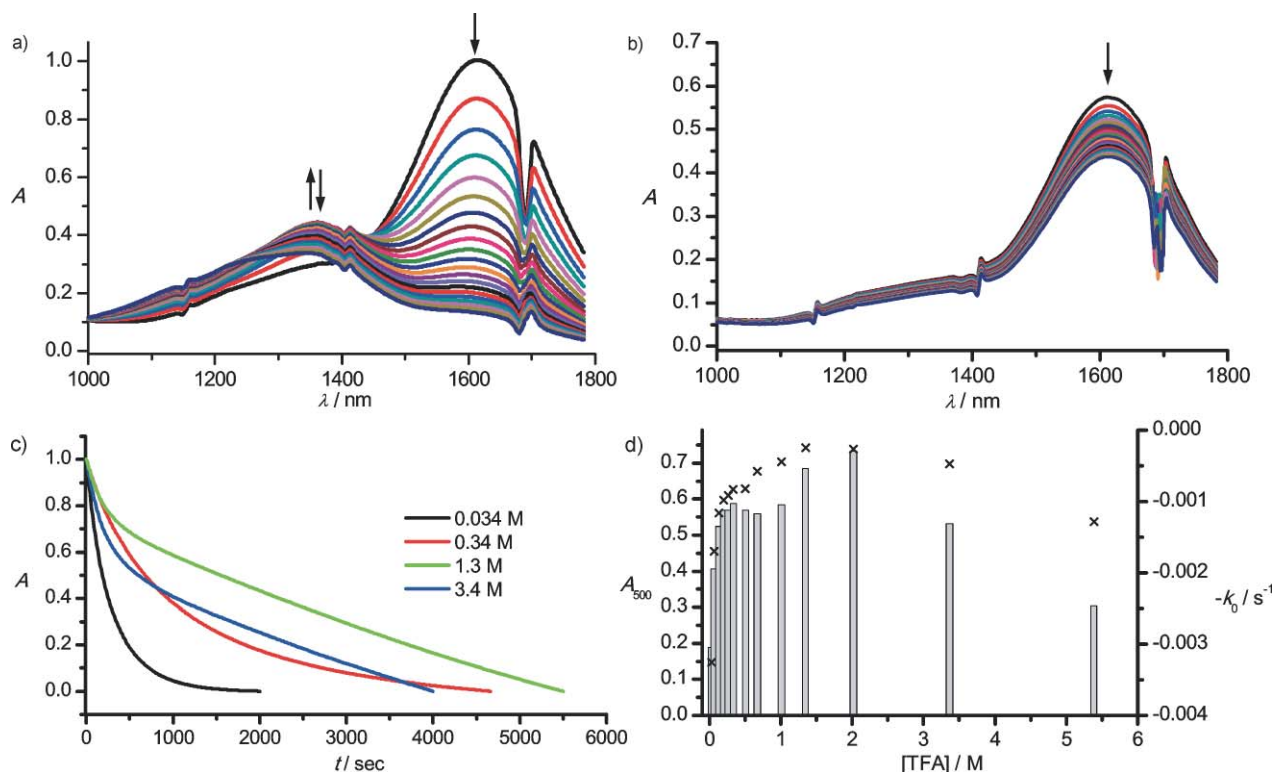
Fig. 7 NIR absorption spectra of cation 8^+ measured at regular intervals in a) CHCl$_3$/2% TFA and b) CHCl$_3$/10% TFA. c) Absorption at λ_{max} plotted over time at different acid concentrations. d) Absorption after 500 s, A_{500}, against acid concentration (bars) and initial rate of reaction, k_0, against acid concentration (crosses). Initial rates were determined by fitting the data to an exponential decay.

7.99 (2H, dd, J = 7.8, 1.5 Hz), 7.86 (4H, d, J = 1.7 Hz), 7.74 (2H, t, J = 1.7 Hz), 7.64–7.70 (3H, m), 1.49 (36H, s), 1.44–1.46 (9H, m), 1.36–1.38 (12H, m), 0.84–0.95 (12H, m), 0.77–0.81 (6H, m); ^{13}C NMR (125 MHz, CDCl$_3$) δ 149.1, 145.9, 143.7, 142.4, 140.1, 139.4, 133.7, 133.5, 132.4, 132.4, 131.2, 128.9, 127.8, 126.9, 121.4, 121.3, 120.9, 96.3, 91.9, 89.7, 81.7, 35.0, 33.2, 31.7, 31.6, 23.9, 22.7, 14.2, 13.3; m/z (MALDI-TOF, +ve) 1149.97 (C$_{76}$H$_{94}$N$_4$NiSi requires 1149.66).

[5,15-bis(3,5-di-*tert*-butylphenyl)-10-phenyl-20-hexatriynyl porphinato] nickel(II) 4

Butadiyne porphyrin **3** was deprotected by the general method. The deprotected porphyrin (0.020 g, 0.023 mmol) and trihexylsi-lylacetylene (0.18 mL, 0.46 mmol) were dissolved in CH$_2$Cl$_2$ (10 mL) and THF (5 mL) and stirred vigorously in a 500 mL flask fitted with a CaCl$_2$ drying tube under air. After 20 min, cop-per(I) chloride (0.068 g, 0.69 mmol) and N,N,N',N'-tetramethyl ethylenediamine (0.079 mL, 0.53 mmol) were added, and the reaction stirred for 4 h. The mixture was passed through a silica plug, before further chromatography (40–60 °C petroleum ether/CH$_2$Cl$_2$, 10 : 1) to give the hexatriyne porphyrin **4** as a purple solid (0.026 g, 95%). m.p. > 250 °C; λ_{max} (CHCl$_3$)/nm (log ε) 441 (5.40), 552 (4.14), 590 (4.36); ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.43 (2H, d, J = 4.8 Hz), 8.84 (2H, d, J = 4.8 Hz), 8.70 (2H, d, J = 4.8 Hz), 8.67 (2H, d, J = 4.8 Hz), 7.98 (2H, d, J = 6.0 Hz), 7.85 (4H, d, J = 1.7 Hz), 7.75 (2H, t, J = 1.7 Hz), 7.64–7.70 (3H, m), 1.49 (36H, s), 1.28–1.47 (21H, m), 0.91–0.95 (9H, m), 0.84–0.89 (3H, m), 0.69–0.73 (6H, m); ^{13}C NMR (125 MHz, CDCl$_3$) δ 149.1, 146.2, 143.9, 142.5, 142.4, 140.6, 130.3, 133.9, 133.5, 132.5, 132.4, 130.1, 128.8, 127.9, 126.9, 121.7, 121.4, 121.4, 95.3, 89.7, 89.3, 81.6, 77.9, 69.8, 68.0, 62.1, 35.0, 33.1, 31.7, 31.5, 23.8, 22.6, 14.2, 13.1; m/z (MALDI-TOF, +ve) 1173.37 (C$_{78}$H$_{94}$N$_4$NiSi requires 1173.67).

[5,15-bis(3,5-di-*tert*-butylphenyl)-10-phenyl-20-[ethynyl-*p*-(trimethylsilylethynyl)phenyl] porphinato] nickel(II) 10

Sonogashira coupling was carried out following a reported procedure.[36] Acetylene porphyrin **2** was deprotected by the general method. The deprotected porphyrin (0.035 g, 0.041 mmol), trimethylsilylethynyl bromobenzene **9** (0.104 g, 0.410 mmol), tris(dibenzylideneacetone)-dipalladium(0) (1.9 mg, 2.1 µmol), triphenylphosphine (1.1 mg, 4.1 µmol) and copper(I) iodide (0.4 mg, 2.1 µmol) were dissolved in dry toluene (1 mL) and triethylamine (1 mL) and the solution was freeze-thaw degassed. The reaction was stirred at 40 °C for 2 h. The crude mixture was passed through a short silica plug (CH$_2$Cl$_2$) before further purification by column chromatography (40–60 °C petroleum ether/CH$_2$Cl$_2$; 5 : 1) to give a red/purple solid (0.020 g, 48%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.58 (2H, d, J = 4.8 Hz), 8.87 (2H, d, J = 4.8 Hz), 8.72 (2H, d, J = 4.8 Hz), 8.68 (2H, d, J = 4.8 Hz), 7.99 (2H, dd, J = 7.9, 1.5 Hz), 7.87–7.89 (6H, m), 7.74 (2H, t, J = 1.9 Hz), 7.64–7.68 (4H, m), 7.62 (2H, d, J = 8.5 Hz), 1.50 (36H, s), 0.32 (9H, s); ^{13}C NMR (125 MHz, CDCl$_3$) δ 149.1, 144.6, 143.4, 142.6, 142.5, 139.5, 133.5, 133.3, 132.4, 132.2, 132.2, 131.3, 131.1, 128.9, 127.8, 126.8, 123.9, 123.0, 121.3, 121.2, 120.3, 104.8, 98.3, 96.5, 96.5, 92.4, 34.9, 31.6, −0.1; m/z (MALDI-TOF, +ve) 1015.29 (C$_{67}$H$_{68}$N$_4$NiSi requires 1014.46).

---

bands are more intense and narrower than charge-transfer type transitions in this region.[31,32]

Experimental Section

Reactions were carried out under nitrogen or argon atmospheres, unless otherwise stated. Copper(I) chloride was freshly prepared from copper(II) chloride.[33] Trihexylsilylacetylene,[34] trimethylsi-lylethynyl bromobenzene **9**[35] and formyl porphyrin **12**[26] were synthesised by published procedures. Ethynyl porphyrin **2** was prepared as in previous work.[21] Dry toluene and THF were obtained by passing through a column of activated alumina. Triethylamine was freshly distilled from CaH$_2$. All other reagents were used as supplied.

Column chromatography was carried out on silica gel 60 under a positive pressure of nitrogen. Where mixtures of solvents were used, ratios are reported by volume.

NMR spectra were recorded at 300 K using a Brucker DPX400 (400 MHz) spectrometer. Spectra recorded on the Brucker AVANCE AVC500 (500 MHz) spectrometer were recorded by Dr B. Odell. Chemical shifts are quoted as parts per million (ppm) relative to tetramethylsilane (0.00 ppm). Coupling constants (J) are quoted in Hertz (Hz). UV-Vis spectra were recorded in solution on a Perkin-Elmer lambda 20 UV-Vis spectrometer. UV-Vis-NIR absorption spectra were recorded in solution using a JASCO V-570 spectrometer. Mass spectra were measured by matrix assisted laser desorption ionisation—Time of Flight (MALDI-TOF) using a Micromass LCT premier spectrometer. Dithranol (1,8-dihydroxy-9,10-dihydroanthracen-9-one) was used as the matrix. Only molecular ions and major peaks are given.

Silyl deprotections—general method

Alkynyl porphyrins were stored and characterised as the silyl protected compounds. Before reaction, the silyl group was re-moved. The silyl protected porphyrin (0.055 mmol) was dissolved in CH$_2$Cl$_2$ (6 mL). Tetrabutylammonium fluoride (1.0 M in THF, 0.06 mL, 0.06 mmol) was added and the reaction stirred for 15 min. The crude reaction mixture was poured onto a silica plug and eluted with CH$_2$Cl$_2$. Removal of solvents gave the free acetylene in quantitative yield, which was characterised only by TLC analysis before the silica plug.

[5,15-bis(3,5-di-*tert*-butylphenyl)-10-phenyl-20-butadiynyl porphinato] nickel(II) 3

Glaser–Hay coupling was achieved by a literature procedure.[24,25] Acetylene porphyrin **2** was deprotected by the general method. The deprotected porphyrin (0.10 g, 0.12 mmol) and trihexylsily-lacetylene (0.93 mL, 2.4 mmol) were dissolved in CH$_2$Cl$_2$ (50 mL) and THF (25 mL) and stirred vigorously in a 1 L flask fitted with a CaCl$_2$ drying tube under air. After 20 min, copper(I) chloride (0.36 g, 3.6 mmol) and N,N,N',N'-tetramethyl ethylenediamine (0.42 mL, 2.8 mmol) were added, and the reaction stirred for 4 h. The mixture was passed through a silica plug, before further chromatography (40–60 °C petroleum ether/CH$_2$Cl$_2$, 10 : 1) to give the butadiyne porphyrin **3** as a purple solid (0.025 g, 91%). m.p. > 250 °C; λ_{max} (CHCl$_3$)/nm (log ε) 435 (5.38), 548 (4.17), 584 (4.16); ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.49 (2H, d, J = 4.9 Hz), 8.85 (2H, d, J = 4.9 Hz), 8.70 (2H, d, J = 4.9 Hz), 8.67 (2H, d, J = 4.9 Hz),

---

[5,15-bis(3,5-di-*tert*-butylphenyl)-10-phenyl-20-(ethynylphenone) porphinato] nickel(II) 17

Acetylene porphyrin **2** was deprotected by the general method. The deprotected porphyrin (0.020 g, 0.024 mmol) was dissolved in THF (1 mL) and the solution freeze-thaw degassed. *N*-Methoxy-*N*-methylbenzamide (0.014 mL, 0.095 mmol) was added, followed by a solution of lithium bis(trimethylsilyl)amide (1.0 M in THF, 0.095 mL, 0.095 mmol) and the mixture stirred for 1 h at room temperature. The reaction was quenched by addition of aqueous ammonium chloride (5 mL). The product was extracted with CH_2Cl_2 (10 mL), washed with H_2O (3 × 10 mL) and purifed by chromatography on silica (40–60 °C petroleum ether/CH_2Cl_2 4 : 1) to give the product as a purple-green solid (0.019 g, 83%). m.p. > 300 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.63 (2H, d, $J = 4.9$ Hz), 8.93 (2H, d, $J = 4.9$ Hz), 8.73 (2H, d, $J = 4.9$ Hz), 8.69 (2H, d, $J = 4.9$ Hz), 8.58 (2H, d, $J = 8.0$ Hz), 8.00 (2H, d, $J = 7.3$ Hz), 7.87 (4H, d, $J = 1.9$ Hz), 7.66–7.76 (8H, m), 1.50 (36H, s); ^{13}C NMR (125 MHz, CDCl$_3$) δ 178.0, 149.2, 145.9, 144.2, 142.7, 142.4, 140.5, 139.3, 137.8, 134.3, 134.0, 133.5, 132.8, 132.5, 129.6, 128.9, 128.0, 126.9, 122.2, 122.1, 121.5, 95.4, 95.1, 93.6, 35.0, 31.7; *m/z* (MALDI-TOF, +ve) 946.51 ($C_{63}H_{60}N_4NiO$ requires 946.41).

[5,15-bis(3,5-di-*tert*-butylphenyl)-10-phenyl-20-ethynyl porphinato] [5,15-bis(3,5-di-*tert*-butylphenyl)-10-phenyl porphinato] methanolato nickel(II) 13

Acetylene porphyrin **2** was deprotected by the general method. The deprotected porphyrin (0.050 g, 0.059 mmol) and formyl porphyrin **12** (0.010 g, 0.012 mmol) were dissolved in dry THF (1 mL). Lithium bis(trimethylsilyl)amide solution (1.0 M in THF, 0.059 mL, 0.059 mmol) was added and the reaction was stirred at room temperature for 1 h. The reaction was quenched with aqueous ammonium chloride (5 mL), extracted with CH_2Cl_2 (10 mL) and washed with H_2O (3 × 10 mL). The product was purified by column chromatography (40–60 °C petroleum ether/CH_2Cl_2; 2 : 1) to give a purple solid (0.006 g, 30%). m.p. > 300 °C; λ_{max} (CHCl$_3$)/nm (log ε) 421 (5.22), 538 (4.31), 601 (4.15); ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.17 (2H, d, $J = 4.9$ Hz), 9.52 (2H, d, $J = 4.9$ Hz), 9.07 (2H, d, $J = 4.9$ Hz), 8.81 (2H, d, $J = 4.9$ Hz), 8.76–8.79 (4H, m), 8.70–8.74 (4H, m), 8.39 (1H, d, $J = 3.8$ Hz), 8.06 (2H, d, $J = 7.1$ Hz), 8.02 (2H, d, $J = 7.5$ Hz), 7.92 (4H, d, $J = 1.6$ Hz), 7.85 (4H, d, $J = 1.6$ Hz), 7.75–7.78 (4H, m), 7.68–7.72 (6H, m), 3.81 (1H, d, $J = 3.8$ Hz), 1.49–1.51 (72H, overlapping s); ^{13}C NMR (125 MHz, CDCl$_3$) δ 149.0, 149.0, 144.8, 143.4, 142.9, 142.5, 142.3, 142.1, 140.8, 140.6, 139.5, 133.9, 133.5, 133.5, 133.3, 132.5, 132.4, 132.3, 132.1, 129.9, 128.9, 128.7, 127.7, 126.9, 126.8, 121.1, 121.0, 120.4, 90.3, 65.6, 34.9, 34.9, 31.6, 31.6; *m/z* (MALDI-TOF, +ve) 1691.76, 1674.73 ($C_{111}H_{112}N_8Ni_2O$ requires 1690.77, –OH requires 1673.77).

[5,15-bis(3,5-di-*tert*-butylphenyl)-10-phenyl-20-butadiynyl porphinato] [5,15-bis(3,5-di-*tert*-butylphenyl)-10-phenyl porphinato] methanolato nickel(II) 15

Butadiyne porphyrin **3** was deprotected by the general method. The deprotected porphyrin (0.010 g, 0.011 mmol) and formyl porphyrin **12** (0.0062 g, 0.0073 mmol) were dissolved in dry THF (1 mL). Lithium bis(trimethylsilyl)amide solution (1.0 M in THF, 0.044 mL, 0.044 mmol) was added and the reaction was stirred at

room temperature for 1 h. The reaction was quenched with aqueous ammonium chloride (5 mL), extracted with CH_2Cl_2 (10 mL) and washed with H_2O (3 × 10 mL). The product was purified by column chromatography (40–60 °C petroleum ether/CH_2Cl_2; 2 : 1) to give a purple solid (0.008 g, 63%). m.p. > 300 °C; λ_{max} (CHCl$_3$)/nm (log ε) 423 (5.00), 437 (5.05), 542 (4.06), 583 (3.96); ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.81 (2H, d, $J = 4.9$ Hz), 9.37 (2H, d, $J = 4.9$ Hz), 8.97 (2H, d, $J = 4.9$ Hz), 8.75–8.77 (4H, m), 8.72 (2H, d, $J = 4.9$ Hz), 8.66 (2H, d, $J = 4.9$ Hz), 8.65 (2H, d, $J = 4.9$ Hz), 8.00 (2H, dd, $J = 7.1, 2.0$ Hz), 7.96 (2H, dd, $J = 7.5, 1.9$ Hz), 7.92 (1H, d, $J = 3.7$ Hz), 7.87 (4H, d, $J = 1.7$ Hz), 7.81 (4H, d, $J = 1.7$ Hz), 7.71–7.73 (4H, overlapping t), 7.64–7.68 (6H, m), 3.56 (1H, d, $J = 3.7$ Hz), 1.45–1.48 (72H, overlapping s); ^{13}C NMR (125 MHz, CDCl$_3$) δ 149.1, 149.0, 145.6, 143.6, 143.0, 142.4, 142.4, 142.2, 142.1, 141.1, 139.5, 139.4, 133.9, 133.6, 133.5, 133.5, 132.5, 132.4, 132.3, 129.8, 128.8, 126.9, 126.8, 121.4, 121.2, 120.9, 120.4, 82.2, 80.3, 67.9, 34.9, 34.9, 31.6, 31.6; *m/z* (MALDI-TOF, +ve) 1716.07, 1698.98 ($C_{113}H_{112}N_8Ni_2O$ requires 1714.77, –OH requires 1697.77).

[5,15-bis(3,5-di-*tert*-butylphenyl)-10-phenyl-20-butadiynyl porphinato] [5,15-bis(3,5-di-*tert*-butylphenyl)-10-phenyl-20-ethynyl porphinato]benzenemethanolato nickel(II) 18

Butadiyne porphyrin **3** was deprotected by the general method. The deprotected porphyrin (0.010 g, 0.011 mmol) and ethynyl ketone porphyrin **17** (0.007 g, 0.007 mmol) were dissolved in dry THF (1 mL). Lithium bis(trimethylsilyl)amide solution (1.0 M in THF, 0.044 mL, 0.044 mmol) was added and the reaction was stirred at room temperature for 1 h. The reaction was quenched with aqueous ammonium chloride (5 mL), extracted with CH_2Cl_2 (10 mL) and washed with H_2O (3 × 10 mL). The product was purified by column chromatography (40–60 °C petroleum ether/CH_2Cl_2; 2 : 1) to give a purple solid (0.004 g, 30%). m.p. > 300 °C; λ_{max} (CHCl$_3$)/nm (log ε) 434 (5.07), 545 (3.97), 584 (3.90); ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.58 (2H, d, $J = 4.9$ Hz), 9.53 (2H, d, $J = 4.9$ Hz), 8.88 (2H, d, $J = 4.9$ Hz), 8.85 (2H, d, $J = 4.9$ Hz), 8.72 (2H, d, $J = 4.9$ Hz), 8.66–8.72 (6H, m), 8.36 (2H, d, $J = 7.6$ Hz), 7.97–8.01 (4H, m), 7.84–7.86 (8H, m), 7.63–7.73 (14H, m), 7.54 (1H, m), 3.60 (1H, s), 1.47 (36H, s), 1.45 (36H, s); *m/z* (MALDI-TOF, +ve) 1816.11, 1799.05 ($C_{121}H_{116}N_8Ni_2O$ requires 1814.80, –OH requires 1797.80).

bis[5,15-bis(3,5-di-*tert*-butylphenyl)-10-phenyl-20-butadiynyl porphinato]benzenemethanolato nickel(II) 6

Butadiyne porphyrin **3** was deprotected by the general method. The deprotected porphyrin (0.045 g, 0.052 mmol) was dissolved in dry THF (2 mL). Methyl benzoate (3.3 µL, 0.026 mmol) and lithium bis(trimethylsilyl)amide solution (1.0 M in THF, 0.208 mL, 0.208 mmol) was added and the reaction was stirred at room temperature for 1 h. The reaction was quenched with aqueous ammonium chloride (5 mL), extracted with CH_2Cl_2 (10 mL) and washed with H_2O (3 × 10 mL). The product was purified by column chromatography (40–60 °C petroleum ether/CH_2Cl_2; 2 : 1) to give a purple solid (0.030 g, 31%). m.p. > 300 °C; λ_{max} (CHCl$_3$)/nm (log ε) 435 (5.65), 549 (4.52), 585 (4.57); ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.53 (4H, d, $J = 4.8$ Hz), 8.87 (4H, d, $J = 4.8$ Hz), 8.71 (4H, d, $J = 4.8$ Hz), 8.67 (4H, d, $J = 4.8$ Hz), 8.12 (2H, d, $J = 8.1$ Hz),

7.99 (4H, dd, J = 7.3, 1.5 Hz), 7.85 (8H, d, J = 1.5 Hz), 7.74 (4H, t, J = 1.5 Hz), 7.64–7.70 (6H, m), 7.61 (2H, dd, J = 7.3 Hz, 8.1 Hz), 7.52 (1H, t, J = 7.3 Hz), 3.38 (1H, s), 1.48 (72H, s); ^{13}C NMR (125 MHz, CDCl$_3$) δ 149.1, 145.8, 143.8, 142.5, 142.4, 140.6, 139.4, 133.9, 133.5, 132.5, 132.4, 131.1, 129.4, 128.9, 128.9, 127.9, 126.9, 126.2, 121.7, 121.3, 121.2, 95.5, 82.5, 82.3, 79.9, 71.9, 66.6, 35.0, 31.7; m/z (MALDI-TOF, +ve) 1840.05, 1823.06 (C$_{123}$H$_{116}$N$_8$Ni$_2$O requires 1838.80, –OH requires 1821.80).

bis[5,15-bis(3,5-di-*tert*-butylphenyl)-10-phenyl-20-[ethynyl-*p*-(trimethylsilylethynyl)phenyl]porphinato] benzenemethanolato nickel(II) 11

Porphyrin **10** was deprotected by the general method. The deprotected porphyrin (7.0 mg, 7.4 µmol) was dissolved in dry THF (1 mL). Methyl benzoate (0.5 µL, 3.7 µmol) and lithium bis(trimethylsilyl)amide solution (1.0 M in THF, 0.030 mL, 0.030 mmol) was added and the reaction was stirred at room temperature for 1 h. The reaction was quenched with aqueous ammonium chloride (5 mL), extracted with CH$_2$Cl$_2$ (10 mL) and washed with H$_2$O (3 × 10 mL). The product was purified by column chromatography (40–60 °C petroleum ether/CH$_2$Cl$_2$; 2 : 1) to give a purple solid (0.002 g, 14%). m.p. > 300 °C; λ_{max} (CHCl$_3$)/nm (log ε) 440 (5.61), 548 (4.46), 587 (4.51); ^{1}H NMR (400 Hz, CDCl$_3$) δ 9.59 (4H, d, J = 4.9 Hz), 8.88 (4H, d, J = 4.9 Hz), 8.72 (4H, d, J = 4.9 Hz), 8.68 (4H, d, J = 4.9 Hz), 8.04 (2H, d, J = 7.5 Hz), 8.00 (4H, dd, J = 7.7, 1.5 Hz), 7.93 (4H, d, J = 8.2 Hz), 7.88 (8H, d, J = 1.8 Hz), 7.65–7.75 (16H, m), 7.52–7.56 (2H, m), 7.45–7.48 (2H, m), 3.18 (1H, s), 1.50 (72H, s); m/z (MALDI-TOF, +ve) 1991.52, 1974.59 (C$_{135}$H$_{124}$N$_8$Ni$_2$O requires 1990.56, –OH requires 1973.56).

Procedure for stability experiments

The stability of the cationic species in solution was investigated by UV/Vis spectroscopy. Trifluoroacetic acid (Acros) and chloroform (Fisher, stabilised with 100 ppm amylene) were used as supplied. A stock solution of the precursor was prepared in CHCl$_3$. 10 µL of this solution was added to a cuvette containing 3 mL of CHCl$_3$. 10 µL of trifluoroacetic acid was added and the absorption at 1611 nm was measured every 10 s in time course measurement mode. This procedure was repeated while varying the concentration of the acid. The initial absorbance was around 0.5, but to directly compare different conditions, each data set was normalised.

Acknowledgements

References

1 J.-L. Brédas, C. Adant, P. Tackx, A. Persoons and B. M. Pierce, *Chem. Rev.*, 1994, **94**, 243–278.
2 A. Bahtiar, K. Koynov, Y. Mardiyati, H.-H. Horhold and C. Bubeck, *J. Mater. Chem.*, 2009, **19**, 7490–7497.
3 G. Stegeman and E. Wright, *Opt. Quantum Electron.*, 1990, **22**, 95–122.
4 C. Fuentes-Hernandez, G. Ramos-Ortiz, S.-Y. Tseng, M. P. Gaj and B. Kippelen, *J. Mater. Chem.*, 2009, **19**, 7394–7401.
5 C. Halvorson, A. Hays, B. Kraabel, R. Wu, F. Wudl and A. J. Heeger, *Science*, 1994, **265**, 1215–1216.
6 J. M. Hales, M. Cozzuol, T. E. O. Screen, H. L. Anderson and J. W. Perry, *Opt. Express*, 2009, **17**, 18478–18488.
7 J. W. Perry, K. Mansour, I. Y. S. Lee, X. L. Wu, P. V. Bedworth, C. T. Chen, D. Ng, S. R. Marder, P. Miles, T. Wada, M. Tian and H. Sasabe, *Science*, 1996, **273**, 1533–1536.
8 C. Kohl, S. Becker and K. Müllen, *Chem. Commun.*, 2002, 2778–2779.
9 C.-L. Mai, W.-K. Huang, H.-P. Lu, C.-W. Lee, C.-L. Chiu, Y.-R. Liang, E. W.-G. Diau and C.-Y. Yeh, *Chem. Commun.*, 2010, **46**, 809–811.
10 J. Fabian, H. Nakazumi and M. Matsuoka, *Chem. Rev.*, 1992, **92**, 1197–1226.
11 J. Fabian and R. Zahradník, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 677–694.
12 N. Sprutta, M. Siczek, L. Latos-Grażynski, M. Pawlicki, L. Szterenberg and T. Lis, *J. Org. Chem.*, 2007, **72**, 9501–9509.
13 I. M. Blake, A. Krivokapic, M. Katterle and H. L. Anderson, *Chem. Commun.*, 2002, 1662–1663.
14 I. M. Blake, L. H. Rees, T. D. W. Claridge and H. L. Anderson, *Angew. Chem., Int. Ed.*, 2000, **39**, 1818–1821.
15 H. S. Gill, M. Harmjanz, J. Santamaría, I. Finger and M. J. Scott, *Angew. Chem., Int. Ed.*, 2004, **43**, 485–490.
16 K. Kurotobi, K. S. Kim, S. B. Noh, D. Kim and A. Osuka, *Angew. Chem., Int. Ed.*, 2006, **45**, 3944–3947.
17 N. G. Pschirer, C. Kohl, F. Nolde, J. Qu and K. Müllen, *Angew. Chem., Int. Ed.*, 2006, **45**, 1401–1404.
18 G. Qian, B. Dai, M. Luo, D. Yu, J. Zhan, Z. Zhang, D. Ma and Z. Y. Wang, *Chem. Mater.*, 2008, **20**, 6208–6216.
19 M. Casalboni, F. De Matteis, P. Prosposito, A. Quatela and F. Sarcinelli, *Chem. Phys. Lett.*, 2003, **373**, 372–378.
20 A. Tsuda and A. Osuka, *Science*, 2001, **293**, 79–82.
21 K. J. Thorley, J. M. Hales, H. L. Anderson and J. W. Perry, *Angew. Chem., Int. Ed.*, 2008, **47**, 7095–7098.
22 T. E. O. Screen, I. M. Blake, L. H. Rees, W. Clegg, S. J. Borwick and H. L. Anderson, *J. Chem. Soc., Perkin Trans. 1*, 2002, 320–329.
23 S. Ohira, J. M. Hales, K. J. Thorley, H. L. Anderson, J. W. Perry and J.-L. Brédas, *J. Am. Chem. Soc.*, 2009, **131**, 6099–6101.
24 H. L. Anderson, *Inorg. Chem.*, 1994, **33**, 972–981.
25 K. Nakamura, T. Fujimoto, S. Takara, K. Sugiura, H. Miyasaka, T. Ishii, M. Yamashita and Y. Sakata, *Chem. Lett.*, 2003, **32**, 694–695.
26 D. P. Arnold and R. D. Hartnell, *Tetrahedron*, 2001, **57**, 1335–1345.
27 S. Nahm and S. M. Weinreb, *Tetrahedron Lett.*, 1981, **22**, 3815–3818.
28 The extinction coefficients in Table 1 were estimated by assuming that the parent alcohols all have the same extinction coefficients, at Soret maxima, as compound **5**.
29 S. Nakatsuji, K. Nakashima, K. Yamamura and S. Akiyama, *Tetrahedron Lett.*, 1984, **25**, 5143–5146.
30 L. M. Tolbert and X. Zhao, *J. Am. Chem. Soc.*, 1997, **119**, 3253–3258.
31 N. Le Narvor, L. Toupet and C. Lapinte, *J. Am. Chem. Soc.*, 1995, **117**, 7129–7138.
32 C. LeVanda, K. Bechgaard, D. O. Cowan, U. T. Mueller-Westerhoff, P. Eilbracht, G. A. Candela and R. L. Collins, *J. Am. Chem. Soc.*, 1976, **98**, 3181–3187.
33 R. N. Keller and H. D. Wycoff, *Inorg. Synth.*, 1946, **2**, 1.
34 D. Lehnherr, J. Gao, F. A. Hegmann and R. R. Tykwinski, *Org. Lett.*, 2008, **10**, 4779–4782.
35 M. G. Steinmetz, C. Yu and L. Li, *J. Am. Chem. Soc.*, 1994, **116**, 932–943.
36 M. J. Plater, S. Aiken and G. Bourhill, *Tetrahedron*, 2002, **58**, 2405–2413.

This journal is © The Royal Society of Chemistry 2010

Org. Biomol. Chem., 2010, **8**, 3472–3479 | 3479