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Synthesis and photochemistry of free base and zinc tetraaryl porphyrins mono-substituted with tungsten pentacarbonyl *via* a pyridine linker †

Catherine J. Aspley, John R. Lindsay Smith,* Robin N. Perutz* and Daniel Pursche

Department of Chemistry, University of York, York, UK YO10 5DD

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A series of free base and zinc porphyrins, mono *meso*-substituted with a pyridyl group *via* an amide link, have been prepared by stepwise functionalisation of free base tetraphenylporphyrin, H_2tpp. Four [W(CO)$_5$L] (L = pyridyl-porphyrin) complexes have been synthesised; [M{tpp-NHCO-py-W(CO)$_5$}], where M = 2H or Zn, one phenyl group is substituted at the 4-position and the pyridine is substituted at the 3- or 4-position. The spectroscopic data of the [W(CO)$_5$L] complexes have been compared with those of the porphyrin ligands alone and with those of the model compounds, [W(CO)$_5$(3-H$_2$NCO-py)] and [W(CO)$_5$(4-H$_2$NCO-py)]. The UV-Vis spectra of the model compounds show that the MLCT and LF absorption bands overlap and no emission is observed at room temperature in solution. The UV-Vis absorption and emission spectra of the porphyrins with peripheral W(CO)$_5$ are dominated by porphyrin bands. Time-resolved emission was observed from the porphyrin moiety in the [W(CO)$_5$L] complexes and fitted to mono-exponential kinetics to give lifetimes of ≤10 ns for the zinc porphyrins and of *ca.* 22 ns for the free base porphyrins. Transients characteristic of the porphyrin $^3(\pi-\pi^*)$ excited state have been observed by time-resolved absorption and their decay kinetics have been fitted to an appropriate rate law. Long wavelength photolysis of [W(CO)$_5$(3-H$_2$NCO-py)] and [W(CO)$_5$(4-H$_2$NCO-py)] in THF resulted in conversion to [W(CO)$_5$(THF)]. The [W(CO)$_5$L] complexes behaved similarly with photolysis at $\lambda > 395$ nm but were photostable with $\lambda > 495$ nm.

Introduction

Among supramolecular systems those that contain a porphyrin coordinated to a peripheral transition metal complex are of particular interest. While some were designed to mimic electron or energy transfer processes in photosynthesis,[1] others were intended for molecular recognition and related purposes.[2–10] Our goal is to exploit the opportunities of combining a porphyrin and a single metal carbonyl into the same molecule and to investigate intramolecular photochemical interactions between the two chromophores.[11] The metal carbonyl group provides an extra means of characterisation through the intense, structure-sensitive CO-stretching mode. Other examples of porphyrins coordinated to a transition metal carbonyl have the following transition metal carbonyl groups on the periphery of various porphyrins: Cr(CO)$_3$, W(CO)$_5$, RuCl$_2$(DMSO)$_2$CO, Re(CO)$_3$-(halide) and (μ-H)Os$_3$(CO)$_{10}$.[9,12–16] In most, the porphyrin is substituted by several metal carbonyl groups and the majority have not been investigated photochemically. In the only previous report of a porphyrin coordinated to W(CO)$_5$, the porphyrin was substituted with four phosphine groups, each of which was coordinated to a W(CO)$_5$ moiety.[13]

Our aim was to synthesise a series of free base and zinc porphyrins coordinated to a single W(CO)$_5$ unit *via* a pyridyl linker and to investigate interactions between the two chromophores, in both the ground and excited states. To this end, the spectroscopic data and photophysical behaviour of the [W(CO)$_5$L] complexes, where L is a pyridyl-porphyrin, have been compared with those of related tungsten pentacarbonyl complexes in the literature, those of analogous non-porphyrinic tungsten complexes and those of the porphyrin ligands themselves.

In the early 1980s, room temperature emission was reported for [W(CO)$_5$(4-CN-py)], where 4-CN-py is 4-cyanopyridine bound to tungsten *via* the pyridine nitrogen.[17] Subsequently, the reactivities of the different excited states of [M(CO)$_5$(substituted pyridine)] (M = Cr, Mo, W) were studied.[18–22] Complexes such as [W(CO)$_5$(4-X-py)], which have an electron-withdrawing group at the 4-position, tend to have the MLCT excited states at lower energy than the LF excited states and are emissive at room temperature in solution.[19–21] Complexes such as [W(CO)$_5$(py)], [W(CO)$_5$(piperidine)] and [W(CO)$_5$(3-X-py)] (in which the electron-withdrawing substituent X is at the 3-position) have the LF excited states at lower energy than the MLCT excited states, are non-emissive at room temperature in solution and have much higher photosubstitution quantum yields.[20,23]

A systematic strategy for the synthesis of novel porphyrins mono-substituted with transition metal carbonyls has been developed. We have previously reported the synthesis of a porphyrin attached to a rhenium carbonyl unit *via* a bipyridyl linker through an amide bond.[11] By varying the acid chloride used in the amide synthesis, we have adapted this method so that novel porphyrins substituted with pyridyl linkers can be obtained.

Results and discussion

Synthesis

The tungsten pentacarbonyl functionalised porphyrins were synthesised by the reaction sequence shown in Scheme 1. Tetraphenylporphyrin, **1**, was converted into 5-(4-aminophenyl)-10,15,20-triphenylporphyrin **2**, in two steps according to a slight modification of a literature method.[24] Porphyrin **2** was converted into porphyrin **3a** mono-substituted with a pyridyl group by reaction with nicotinoyl chloride hydrochloride (Scheme 1). Metallation of **3a** with zinc acetate led to zinc porphyrin **3b**. Similarly, the porphyrins **4a** and **4b** (Scheme 2)

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† Electronic supplementary information (ESI) available: derivation of eqn. (4), free energy calculations, spectroscopic data in additional solvents. See http://www.rsc.org/suppdata/dt/b1/b108562j/

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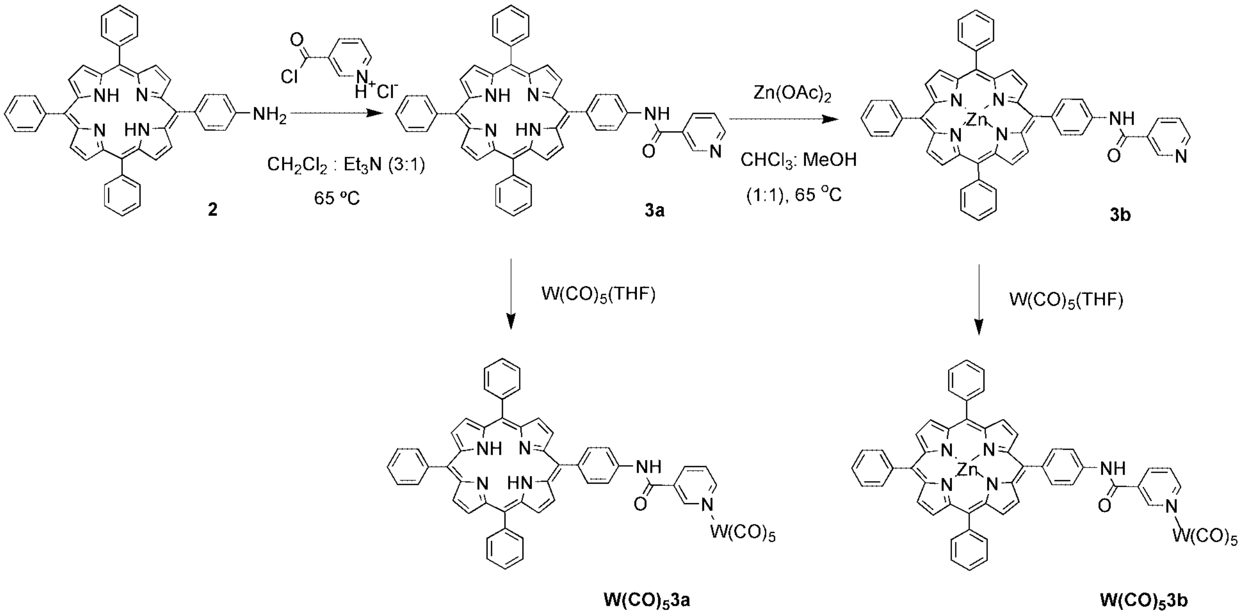
were made by reaction of **2** with isonicotinoyl chloride hydrochloride. Any of these four porphyrin ligands can be coordinated to a single $W(CO)_5$ moiety by a variation of the literature method for the synthesis of $[M(CO)_5$(substituted pyridine)].[17,19,20] One equivalent of $[W(CO)_5(THF)]$ was added to the porphyrin ligand in THF solution and left stirring overnight at room temperature before removal of THF. The complexes $W(CO)_5$**3a**, $W(CO)_5$**3b**, $W(CO)_5$**4a** and $W(CO)_5$**4b** were obtained on recrystallisation (Schemes 1 and 2). They have a perceptibly browner colour than the purple of their parent porphyrins.

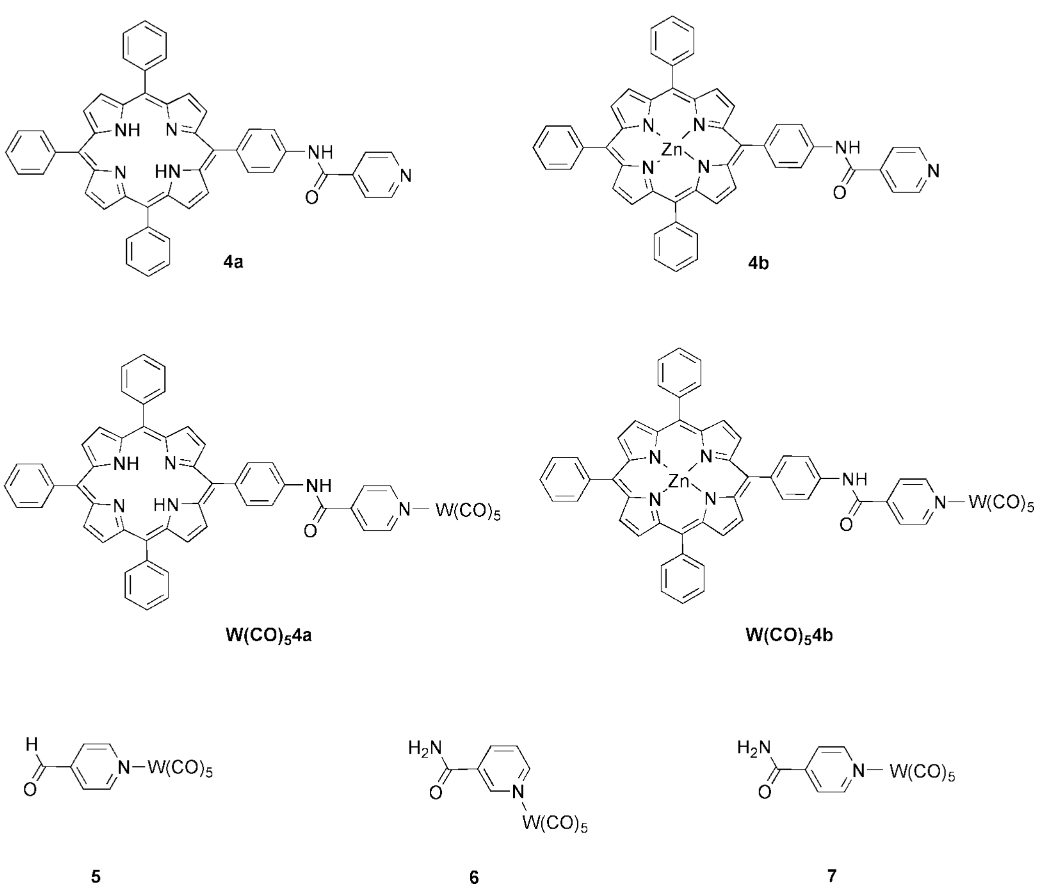
Scheme 2 also illustrates $[W(CO)_5$(4-CHO-py)], **5**, $[W(CO)_5$(nicotinamide)], **6** and $[W(CO)_5$(isonicotinamide)], **7**. Complex **5** was prepared for direct comparison with the literature,[19] while the new compounds **6** and **7** were prepared as they are better models of the tungsten moiety in $W(CO)_5$**3** and $W(CO)_5$**4** than known $W(CO)_5$ derivatives.

Steady-state spectroscopy

The IR spectroscopic data agree with literature values for C_{4v} $M(CO)_5$(substituted-pyridine) complexes (Table 1).[20,23,25,26] The



Scheme 1 The syntheses of **3a**, **3b**, $W(CO)_5$**3a** and $W(CO)_5$**3b**.



Scheme 2 Compounds **4a**, **4b**, $W(CO)_5$**4a**, $W(CO)_5$**4b**, **5**, **6** and **7**.

Table 1 IR data ($\bar{\nu}$/cm^{-1}) for a variety of [M(CO)$_5$L] complexes

Complex	Solvent	a_1^1	b_1	e	a_1^2	Amide/formyl CO
[W(CO)$_5$(THF)]	—	2075 w	—	1929 s	1890 m	
W(CO)$_5$**3a**	Benzene	2072 w	1974 vw	1930 s	≈1910 (sh)	—
	THF	2071 w	1975 vw	1930 s	1900	
W(CO)$_5$**3b**	Benzene	2072 w	1975 vw	1931 s	≈1910 (sh)	—
	THF	2072 w	1974 vw	1930 s	1901	
	CH$_3$CN	2075 w	—	1932 s	1893 m	—
W(CO)$_5$**4a**	Benzene	2071 w	≈1976 vw	1930 s	≈1910 (sh)	—
W(CO)$_5$**4b**	Benzene	2071 w	≈1975 vw	1931 s	≈1910 (sh)	—
	CH$_3$CN	2074 w	—	1933 s	1893 (sh)	—
[W(CO)$_5$(3-CHO-py)]	Nujol	2071 w	—	1930 s	1914	1731
[W(CO)$_5$(4-CHO-py)] (**5**)	Nujol	2070 w	—	1930 s	1914	1734
[W(CO)$_5$(nic)] (**6**)	CH$_2$Cl$_2$	2073 w	1976 vw	1930 s	1899 m	1698 w
[W(CO)$_5$(isonic)] (**7**)	CH$_2$Cl$_2$	2073 w	1974 vw	1931 s	1900 m	1700 w

Table 2 Selected ^{1}H NMR data [δ (J/Hz)] for [W(CO)$_5$L] complexes and for L (L = porphyrin) in [^{2}H$_8$]THF. Spectra recorded at 300 MHz

W(CO)$_5$**3a**	W(CO)$_5$**3b**	W(CO)$_5$**4a**	W(CO)$_5$**4b**	**3a**	**4a**	**4b**	
10.27 (s, 1H)	10.18 (s, 1H)	10.24 (s, 1H)	10.25 (s, 1H)	10.11 (s, 1H)	10.20 (s, 1H)	10.00 (s, 1H)	amide NH
9.69 (s, 1H)	9.68 (d, *J* 1.8, 1H)	9.33 (d, *J* 5.9, 2H)	9.37 (d, *J* 5.2, 2H)	9.37 (d, *J* 2.2, 1H)			nic/isonic
9.32 (d, *J* 5.5, 1H), 8.66 (d, *J* 7.4, 1H)	9.29 (dd, *J* 5.2, *J* 1.1, 1H)			8.88 (dd, *J* 4.8, *J* 1.5, 1H)	9.03 (d, *J* 4.8, 2H)	8.43^{a} (d, *J* 6.2, 2H)	
7.75 (dd, *J* 7.4, *J* 1.5, 1H)	8.62 (dt, *J* 8.1 Hz, *J* 1.8, 1H) 7.71 (ddd, *J* 8.1, *J* 5.5, *J* 1.1, 1H)	8.08 (d, *J* 5.9, 2H)	8.13 (d, *J* 5.2, 2H)	8.48 (dt, *J* 7.7, *J* 2.2, 1H) 7.62 (dd, *J* 7.7, *J* 4.5, 1H)	8.04 (m, 2H)	7.91^{a} (d, *J* 6.2, 2H)	
9.02–8.96 (m, 8H)	9.02 (d, *J* 4.6, 2H), 8.97 (d, *J* 4.6, 2H), 8.95 (s, 4H)	8.99–8.91 (d, *J* 4.4 Hz & m, 8H)	9.04–8.97 (m, 8H)	9.04 (d, *J* 4.8, 2H), 8.95 (m, 6H)	8.94 (m, 8H)	9.02 (d, *J* 4.4, 2H), 8.98–8.96 (m, 6H)	*β*-pyrrole
8.35–8.30 (m, 10H)	8.35–8.25 (m, 10H)	8.31–8.28 (m, 10H)	8.33 (m, 10H)	8.40–8.31 (m, 10 H)	8.39–8.33 (m, 10H)	8.34–8.30 (m, 10H)	bridging/ *o*-phenyl
7.90 (m, 9H)	7.84 (m, 9H)	7.85 (m, 9H)	7.88 (s, 9H)	7.88 (m, 9H)	7.91 (m, 9H)	7.87–7.84 (m, 9H)	*m*-/*p*-phenyl
−2.57 (s, 2H)	N/A	−2.58 (s, 2H)	N/A	−2.53 (s, 2H)	−2.58 (s, 2H)	N/A	pyrrole NH

^{a} Concentration dependent.

^{1}H NMR spectra of the [W(CO)$_5$L] complexes were recorded in [^{2}H$_8$]THF and compared to the spectra of porphyrins before coordination to the W(CO)$_5$ moiety (Table 2). In all cases, the resonances due to the porphyrin macrocycle (the *β*-pyrrole, the *ortho*-phenyl and the *meta*-/*para*-phenyl resonances at *ca.* δ 9.0, 8.3 and 7.9 respectively), were barely changed on coordination to the tungsten carbonyl unit. However, the resonances due to the protons on the pyridine ring and the amide proton were shifted to lower field by up to δ 0.4 (Fig. 1). Shifts to lower field of up to δ 0.4 were also observed in the ^{1}H NMR spectrum of nicotinamide on coordination to the W(CO)$_5$ moiety to give **6**. The shifts are in agreement with the presumption that the ground state dipole moment of [W(CO)$_5$(4-X-pyridine)] complexes is directed from the pyridine ligand to the tungsten fragment as a result of donation of electron density from the pyridine nitrogen lone pair into the empty tungsten d_{z^2} orbital.[27]

The ^{13}C{^{1}H} NMR spectra of all the [W(CO)$_5$L] compounds, where L = porphyrin, were recorded in [^{2}H$_8$]THF (Table 3). The W(CO)$_5$ moiety is characterised by resonances at *ca.* δ 204 (*trans* CO) and 201 (*cis* CO) in a ratio of approximately 1 : 4.[28–30] A thorough assignment of the ^{13}C{^{1}H} NMR spectra was made using ^{1}H-^{13}C COSY NMR spectroscopy. Comparison of the spectra of W(CO)$_5$**4b** and **4b** (Table 3), shows that the isonicotinoyl resonances are shifted to lower field by up to δ 7.

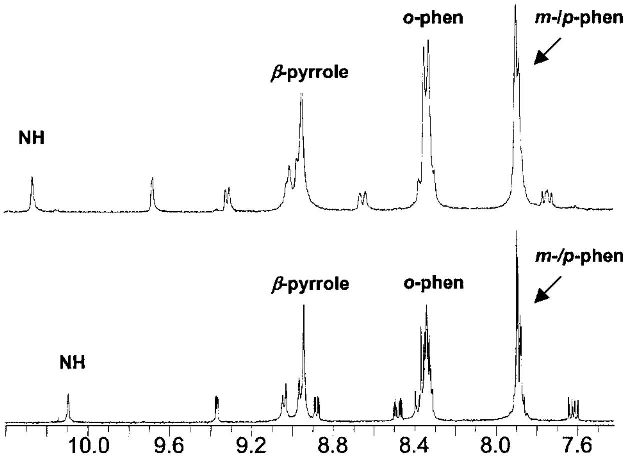


Fig. 1 ^{1}H NMR spectra recorded in [^{2}H$_8$]THF at 300 MHz of W(CO)$_5$**3a** (top) and **3a** (bottom). The amide NH, *β*-pyrrole, *o*-phen and *m*-/*p*-phen resonances are marked. The other resonances are due to protons on the nicotinamide ring.

In agreement with the literature, the UV-Vis spectrum of **5** in methylcyclohexane clearly shows the long wavelength absorption band at 471 nm with a shoulder at *ca.* 510 nm due to the MLCT transitions.[19,23] LF bands are observed at 333 ($e^4b_2^2 \longrightarrow e^3b_2^2b_1^1$), and 401 nm ($e^4b_2^2 \longrightarrow e^3b_2^2a_1^1$).[20] In more polar solvents such as benzene, the MLCT band blue-shifts (negative solvatochromism) to overlap with the LF transition to give a maximum at 401 nm (literature 402 nm) with a shoulder at 430 nm.[19]

The UV-Vis spectra of **6** and **7** were recorded in benzene or THF, or in mixed solvent systems, since the complexes are insoluble in non-polar solvents (Fig. 2). No evidence of a

Table 3 Selected ^{13}C {^{1}H} and ^{1}H-^{13}C COSY NMR data (δ) for [W(CO)$_5$(porphyrin)] complexes in [$^{2}H_8$]THF. The values in brackets refer to the corresponding resonance in the ^{1}H NMR spectrum

W(CO)$_5$**3a**	W(CO)$_5$**3b**	W(CO)$_5$**4a**	W(CO)$_5$**4b**	**4b**	
203.6	203.7	203.9	203.9	N/A	*trans* CO
201.0	201.0	201.0	200.9	N/A	*cis* CO
164.4	164.4	164.7	164.6	166.0	amide CO
157.6 (9.69)	157.6 (9.68)	159.2 (9.33)	159.2 (9.37)	152.2 (8.43[a])	nic or isonic
160.3 (9.32)	160.3 (9.29)			123.2 (7.9[a])	
138.8 (8.66)	138.8 (8.62)	125.7 (8.08)	125.7 (8.13)		
127.6 (7.75)					
132.8 (br, w)[b]	133.5	132 (br, w)[b]	133.4	133.4	β-pyrrole
	133.3		133.3		
137.0	137.0	137.0	136.9	136.8	bridging or
136.5	136.6	136.5	136.6	136.5	*ortho*-phenyl
120.4	120.1	120.4	120.0	119.9	
129.8	129.3	129.8	129.3	129.3	*meta*-/*para*-phenyl
128.8	128.4	128.8	128.4	128.3	
	127.6				

[a] Concentration dependent. [b] Shows a weak cross-peak in the ^{1}H-^{13}C COSY NMR spectra with the β-pyrrole.

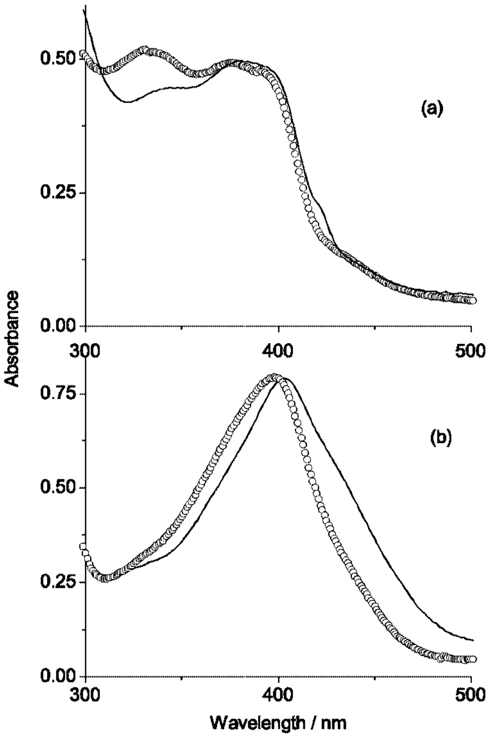


Fig. 2 UV-Vis absorption spectra of (a) **6** in THF : cyclohexane (1 : 5) (—) and THF (°°°) and (b) **7** in benzene : cyclohexane (1 : 9) (—) and benzene (°°°). The spectra were scaled to have the same maximum absorbance in the different solvent systems.

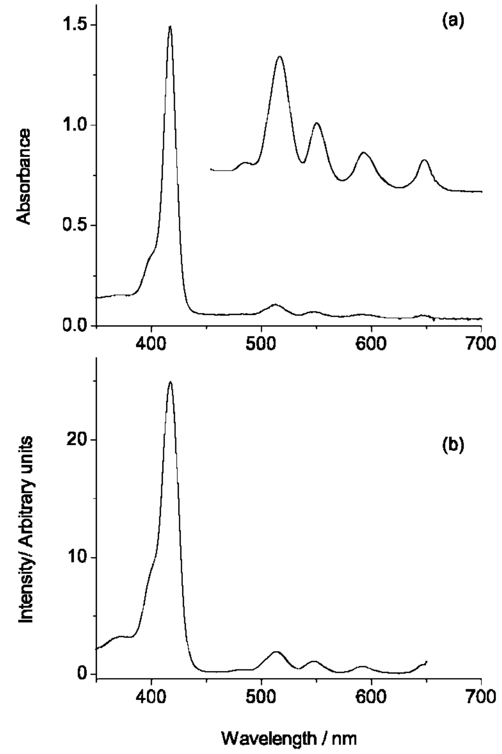


Fig. 3 (a) UV-Vis absorption spectrum and (b) excitation spectrum (emission wavelength 650 nm) of W(CO)$_5$**3a** in THF. The inset shows an expansion of the Q-band region.

long-wavelength MLCT band was seen for either complex, even when the mixture contained a high proportion of a non-polar solvent. The lack of low energy MLCT band was expected for **6** since the substituent lies at the 3-position,[20] but was unanticipated for **7** which has the electron-withdrawing CONH$_2$ group in the 4-position.[31] A quantitative comparison of electron-withdrawing character can be made by studying modified Hammett substituent constants, σ^0.[32] The substituents CONH$_2$, CN and CHO have $\sigma_p{}^0$ values of 0.31, 0.71 and 0.47 respectively, showing that a CONH$_2$ substituent is less electron-withdrawing than a cyano or formyl substituent.[32] It appears, therefore, that the electron-withdrawing capability of the CONH$_2$ group is such that the MLCT band overlaps with the LF bands [*cf.* [W(CO)$_5$(piperidine)][21,23] or [W(CO)$_5$(3,5-pyBr$_2$)].[23]

The UV-Vis spectra of [W(CO)$_5$L], where L = porphyrin, are dominated by porphyrin transitions (Table 4, Fig. 3a). Although there is no shift in the position of the UV-Vis absorption bands, peripheral metallation with W(CO)$_5$ causes a reduction in the absorption coefficients of the Soret bands as has been reported for the peripheral metallation of other porphyrins.[6b] No tungsten-based absorption could be detected for the [W(CO)$_5$L] complexes where L = porphyrin. For both W(CO)$_5$**3** and W(CO)$_5$**4**, the MLCT bands are expected to overlap with the LF bands by comparison with **6** and **7**. In either THF or benzene, the wavelength maximum would be *ca.* 390 to 400 nm, where the Soret band begins to absorb strongly. Considering that the absorption coefficient of a porphyrin at *ca.* 400 nm in THF, on the edge of the Soret band absorption, is in the range 40 000 to 80 000 dm^3 mol^{-1} cm^{-1}, compared to a value of

Table 4 UV-Vis spectroscopic data for [W(CO)$_5$L] complexes and for L (L = porphyrin)

		λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})					
Porphyrin	Solvent	Soret	sh	Q	Q	Q	Q
W(CO)$_5$**3a**	Benzene	420	—	515	550	591	648
	THF	417 (403000)	482 (3880)	513 (15800)	548 (8430)	591 (5210)	648 (4430)
W(CO)$_5$**3b**	Benzene	424	—	513	549	589	—
	THF	423 (549000)	—	517 (3640)	555 (18700)	595 (7640)	—
W(CO)$_5$**4a**	Benzene	420	481	515	550	592	647
	THF	417	480	513	547	590	647
W(CO)$_5$**4b**	Benzene	423	—	513	550	589	—
	THF	423		513	556	595	
3a	Benzene	418	482	514	548	590	647
	THF	417 (490000)	482 (4520)	513 (19800)	548 (10700)	591 (6620)	647 (4780)
3b	THF	422 (618000)	—	516 (4100)	554 (19800)	596 (8330)	—
4a	THF	417	482	513	547	591	647
4b	THF	424	—	517	556	596	—

Table 5 Emission data (300 K) for [W(CO)$_5$L] complexes and for L (L = porphyrin)

			Emission λ_{max}/nm			
			Uncorrected		Corrected	
Porphyrin	Solvent	λ_{ex}/nm	Q(0,0)	Q(0,1)	Q(0,0)	Q(0,1)
W(CO)$_5$**3a**	THF	355, 390 or 513	650		652	*ca.* 710
W(CO)$_5$**3b**	THF[a]	435 or 445	603	650	605	655
W(CO)$_5$**4a**	THF	355 or 513	650		652	710
W(CO)$_5$**4b**	THF[a]	556	602	650	605	655
	Benzene	435	600	643	603	649
3a	THF	513	650		652	*ca.* 710
3b	THF	355 or 435	603	650	606	656
4a	THF	513	650		652	*ca.* 710
4b	THF	355 or 435	602	651	605	655
	Benzene	435	600	643	603	648

[a] For W(CO)$_5$**3b** and W(CO)$_5$**4b** after prolonged exposure to the excitation beam at 435 or 445 nm, extra bands were observed at *ca.* 620 nm (uncorrected) and at 628 nm (corrected).

5070 dm^3 mol^{-1} cm^{-1} for the 378 nm band in the absorption spectrum of **6**, it is not unexpected that the tungsten-based absorption is masked.

Photochemistry and photophysics

The effect of photolysis on **6**, **7**, the [W(CO)$_5$L] complexes and the porphyrin ligands themselves was investigated. Steady-state photolysis of THF solutions of **6** and **7**, using cut-off filters with $\lambda > 375$ or $\lambda > 420$ nm, led to the formation of the same product with a maximum at 418 nm that is readily assigned as [W(CO)$_5$(THF)]. Usually [W(CO)$_5$(4-X-pyridine)] complexes, where X is an electron-withdrawing group, have low quantum yields for the substitution of the pyridine ligand, since the MLCT excited state lies lower in energy than the LF excited state.[19] The 3-X analogues or complexes with electron-donating groups, have the LF excited state lowest lying and have higher photosubstitution quantum yields.[23] Complexes **6** and **7** both have the LF excited state lying lowest and so will have relatively high photosubstitution quantum yields.

Photolysis of W(CO)$_5$**3a** or W(CO)$_5$**3b** with a $\lambda > 395$ cut-off filter with monitoring by IR spectroscopy showed evidence for the formation of [W(CO)$_5$(THF)]. Photosubstitution could be prevented by using a $\lambda > 495$ nm cut-off filter such that light was absorbed by the porphyrin Q-bands only. The photosensitivity of these complexes is surprising considering that almost all the light is absorbed by the porphyrin moiety throughout this wavelength range. It is possible that tungsten-based excited states are populated by energy transfer from the porphyrin. In some related systems, there has been concern that metal–pyridine bonds may dissociate in very dilute solutions.[14e] The IR spectra measured for the photolysis experiments demonstrate the integrity of the W–N bond prior to photolysis even with very dilute solutions. Note that a related zinc porphyrin coordinated to Re(CO)$_3$Br *via* a bipyridyl linker showed no evidence of light sensitivity.[11]

The emission spectra of all the model complexes **5**, **6**, and **7** showed weak, broad emission in the solid state with maxima in the range 550 to 580 nm. Emission was observed from [W(CO)$_5$(4-CHO-py)], **5**, in either methylcyclohexane or benzene solutions as in the literature.[19] No emission was observed from **6** or **7** in benzene. The lack of room temperature emission for **6** and **7** is consistent with the lack of lowest energy MLCT excited states.[19]

The emission spectra of the [W(CO)$_5$L] compounds (Table 5) reveal luminescence for the porphyrins 10–100 fold more intense than that of **5**, **6** or **7**. For W(CO)$_5$**3a** and W(CO)$_5$**4a**, the fluorescence spectra are typical of free base porphyrins with emission at 650 nm in the uncorrected spectra and at 652 [$Q_x(0,0)$] and *ca.* 710 nm [$Q_x(0,1)$] in the corrected spectra (Fig. 4). The intensity of emission from W(CO)$_5$**3a** has been compared with that from **3a** alone by two methods. In the first, the sample of **3a** had the same absorbance at the excitation wavelength of 513 nm as the sample of W(CO)$_5$**3a**; in the second the samples had identical concentrations (Fig. 4).[33–35] In each case, only very small differences in emission intensity were observed which were within the estimated range of experimental error. The excitation spectrum of W(CO)$_5$**3a** (Fig. 3b) has maxima at 418, 513, 548, 591 and 649 nm and is in good agreement with the UV-Vis spectrum (Fig. 3a). It is important to recognise that the emission spectra of **6** and **7** and of the porphyrin complexes with peripheral W(CO)$_5$, were recorded in THF or benzene, and that such solvents reduce φ_{em} and the emission lifetime for [W(CO)$_5$(substituted pyridine)]

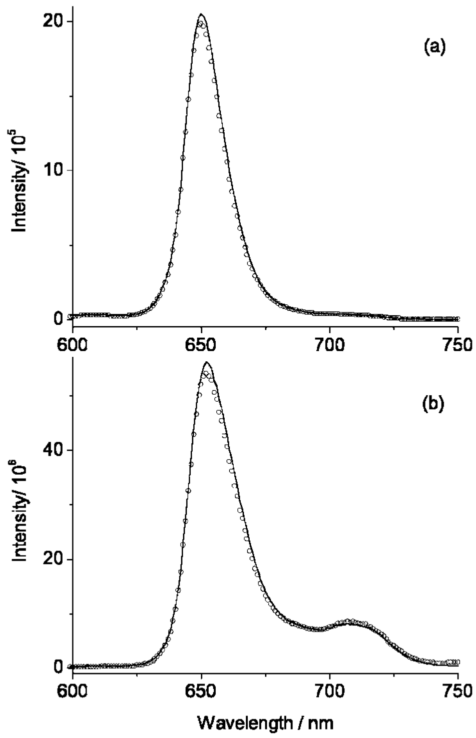


Fig. 4 Emission spectra of **3a** (—) and $W(CO)_5$**3a** (°°°) in THF at the same concentration (2.5×10^{-5} mol dm^{-3}) (a) uncorrected and (b) corrected.

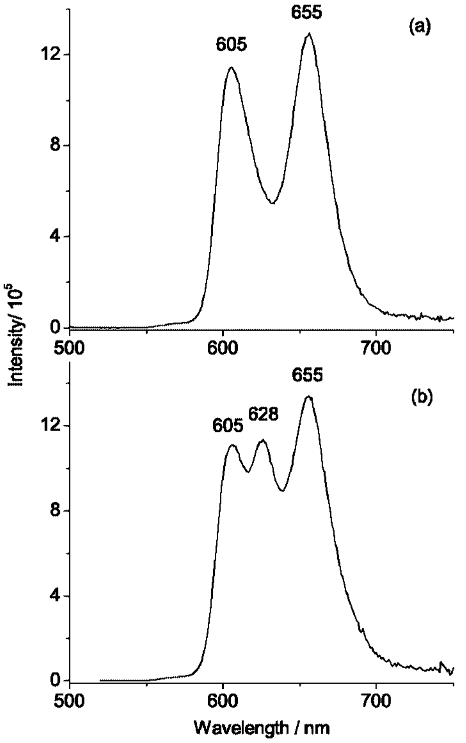


Fig. 5 Corrected fluorescence spectra for $W(CO)_5$**3b** in THF with excitation at 435 nm recorded (a) immediately and (b) after longer exposure to the excitation beam.

complexes relative to values for alkane solvents.[18,19] However, we were unable to record emission spectra of **6**, **7** and the porphyrin complexes in non-polar solvents such as methylcyclohexane since they are too insoluble.

The metalloporphyrins, $W(CO)_5$**3b** and $W(CO)_5$**4b**, exhibit some unusual luminescence behaviour. The emission spectrum of $W(CO)_5$**3b** (with excitation at 435 nm), recorded in THF immediately after preparation of the fluorescence samples is typical of a zinc porphyrin.[14*e*,33,35] The uncorrected emission spectrum has bands at 603 and 650 nm and the corrected emission spectrum has bands at 605 and 655 nm (Fig. 5a). However, after longer exposure to the excitation lamp a new band is observed between the two Q-band emissions. In the spectrum corrected for instrument response, the third band lies at 628 nm (Fig. 5b, Table 5). In the case of $W(CO)_5$**4b**, in THF solution, the third band was not observed immediately with 556 nm excitation but was observed rapidly with excitation at 435 nm.

The extra band in the emission spectra of the zinc porphyrins, $W(CO)_5$**3b** and $W(CO)_5$**4b** must originate in a porphyrin-derived transition on the basis of its intensity and width. A tentative suggestion is that photoinduced electron transfer (eT) occurs, but the precise product has not been identified. Calculations of the free energy, employing literature data for electrochemical potentials, suggest that eT from porphyrin to tungsten is energetically favourable (*ca.* -0.07 V) for the zinc porphyrins, but eT in the opposite direction is favoured for the free base porphyrins (*ca.* -0.08 V, see ESI).† Recent experiments indicate that eT occurs on photolysis of zinc porphyrins with appended $[Re(bpy)(CO)_3(3\text{-}Mepy)]^+$.[36]

Time-resolved emission experiments (λ_{ex} 355 nm) were carried out on **3a** and **3b**, $W(CO)_5$**3a** and $W(CO)_5$**3b**. Emission was observed from the $^1(\pi\text{–}\pi^*)$ excited state of all four porphyrins. No difference was observed between the behaviour of **3a** and $W(CO)_5$**3a** or between that of **3b** and $W(CO)_5$**3b**. The lifetime of the $^1(\pi\text{–}\pi^*)$ excited state is 22 ns in the case of the free base porphyrins and is less than or equal to 10 ns (the width of the excitation pulse) in the case of the metalloporphyrins. Zinc porphyrins usually exhibit lifetimes of *ca.* 2 ns[37–40] while free base aryl porphyrins usually have lifetimes around 10 ns.[7,35–38,41]

The free base porphyrins emit between 600 and 750 nm. There are no differences between the time-resolved spectra which each show two bands at 650 and 720 nm in excellent agreement with the steady-state corrected emission spectra (Fig. 4 and Table 5). The metalloporphyrins emit at higher energy in the region 580 to 700 nm. The spectrum of **3b** is typical of a metalloporphyrin with two emission bands at *ca.* 610 and 650 nm in agreement with the steady-state emission spectrum (Table 5). The time-resolved emission spectrum of $W(CO)_5$**3b** differs from that of **3b** in showing the expected two bands and a third band at 630 nm. The spectrum is very like that obtained after slightly prolonged exposure to the exciting light by steady-state fluorimetry (Fig. 5b).

The $^3(\pi\text{–}\pi^*)$ excited states of **3a**, $W(CO)_5$**3a**, **3b** and $W(CO)_5$**3b** were monitored by time-resolved absorption spectroscopy between 440 and 800 nm on the nano to microsecond timescale. Transient absorption spectra were obtained point-by-point 0.8 μs after the flash for all four porphyrins (Fig. 6). The presence of a $W(CO)_5$ moiety has no effect on the time-resolved absorption spectrum of the porphyrins. Both free base porphyrins, $W(CO)_5$**3a** and **3a**, showed strong transient signals from 440 to *ca.* 480 nm with maxima at *ca.* 440 nm. They both showed bleaching at 520 nm and less intense transient absorption in the Q-band region which extended into the near-infrared. The metalloporphyrins have the short-wavelength maxima at longer wavelength than the free base porphyrins, at *ca.* 460 nm. They also show fewer maxima and minima in the Q-band region and more intense absorption at 780 nm. The transient spectra are typical of porphyrin $^3(\pi\text{–}\pi^*)$ excited states.[7,14*e*,39,42] No time-resolved absorption measurements were carried out on $W(CO)_5$**4b** because of its photosensitivity.

The decays of all the porphyrins fitted better to bi- than mono-exponential kinetics although describing the decay as biexponential is an over-simplification. In fact, the decay is due to competition between first-order decay of the triplet excited state and bimolecular triplet–triplet annihilation reactions [eqns. (1), (2)].[14*e*] The rate of loss of A* is given by

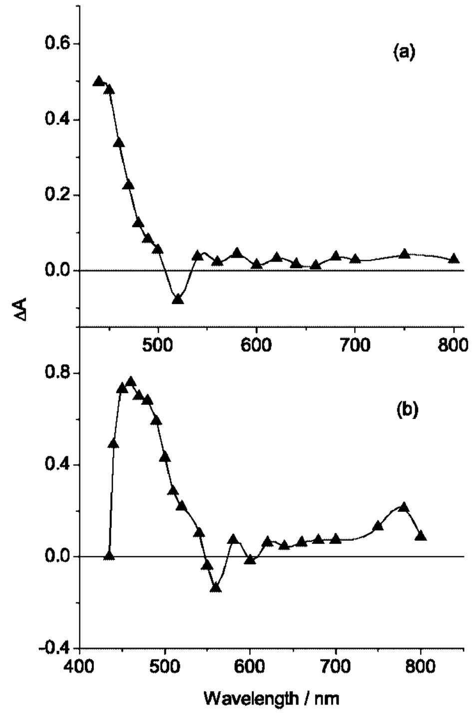


Fig. 6 The transient absorption spectra obtained in THF 0.8 μs after flash of (a) $W(CO)_5$**3a** and (b) $W(CO)_5$**3b**.

eqn. (3) and the integrated form of the rate law by eqn. (4) (see ESI).†

$$A^* \xrightarrow{k_1} A \tag{1}$$

$$A^* + A^* \xrightarrow{k_2} 2A \tag{2}$$

$$\frac{-d[A^*]}{dt} = k_1[A^*] + 2k_2[A^*]^2 \tag{3}$$

$$[A^*]_t = \frac{k_1}{e^{k_1 t}\left(\frac{k_1}{[A^*]_0} + 2k_2\right) - 2k_2} \tag{4}$$

Eqn. (4) is similar to the equation used by Prodi *et al.* for analysing the decay of transients decaying by competing first and second order processes.[14e] The data were fitted to eqn. (4) (Fig. 7) using estimated values for the absorption coefficient of the excited state for each porphyrin. The values were 18 000, 71 000 and 38 000 $dm^3\ mol^{-1}\ cm^{-1}$ which are the reported absorption coefficients of the excited states of a free base porphyrin in THF at 445 nm,[33] and of Zn(tpp) in methylcyclohexane at 470 and 400 nm respectively.[43] The resulting initial excited state concentrations, $[A^*]_0$, lay in the range 9×10^{-6} to 3×10^{-4} mol dm^{-3}. The fits gave a first order rate constant, k_1, of $(5.0 \pm 1.5) \times 10^4\ s^{-1}$ and a second-order rate constant, k_2, of $(0.3 - 5) \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$. The value of k_2 varied according to the absorption coefficient value used. Within experimental error there was no difference in the lifetimes of porphyrin $^3(\pi$–$\pi^*)$ excited states, showing that they were affected neither by the presence of $W(CO)_5$ on the periphery nor by the presence of zinc in the porphyrin. The lifetime data are consistent with values reported for porphyrin triplet excited states.[7,14e,35,40]

Conclusions

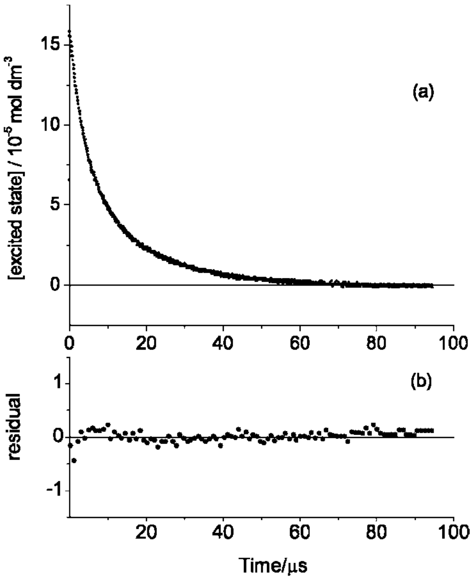


Fig. 7 (a) Experimental change in excited state concentration with time for $W(CO)_5$**3a**. (b) The residuals for the difference between the fit obtained using the integrated rate expression and the experimental data ($\varepsilon_{\text{excited state}} = 18\ 000\ dm^3\ mol^{-1}\ cm^{-1}$).

Four novel porphyrins susbstituted with a peripheral tungsten pentacarbonyl moiety, $W(CO)_5$**3a**, $W(CO)_5$**3b**, $W(CO)_5$**4a** and $W(CO)_5$**4b**, have been synthesised from 5-(4-aminophenyl)-10,15,20-triphenylporphyrin **2** in a systematic fashion and thoroughly characterised by a wide range of techniques. Their photophysical properties have also been investigated in depth and their behaviour compared with those of some new small molecule analogues, **6** and **7**, which are good models for the ordering of the excited states of $W(CO)_5$**3** and $W(CO)_5$**4**. The UV-Vis and solution emission experiments showed no evidence of a low-lying ^{3}MLCT excited state for either **6** or **7**. The UV-Vis spectra of $W(CO)_5$**3a**, $W(CO)_5$**3b**, $W(CO)_5$**4a** and $W(CO)_5$**4b** are dominated by porphyrin transitions. Likewise, the steady-state fluorescence spectra in THF show emission from the porphyrin $^1(\pi$–$\pi^*)$ excited states only. The tungsten moiety has no effect on the lifetime of the porphyrin singlet excited state. The time-resolved absorption spectra are also typical of triplet-state porphyrins. The triplet excited states decayed according to complex kinetics: the lifetime of the $^3(\pi$–$\pi^*)$ excited state is *ca.* 20 μs and triplet–triplet quenching occurs at diffusion control. Time-resolved absorption spectra and kinetics were typical of porphyrins/metalloporphyrins. No evidence of tungsten-based excited states could be observed (the literature reports two transient absorption features at *ca.* 400–460 nm and *ca.* 600 nm for $[W(CO)_5(4\text{-X-py})]$)[19] but most of the excitation energy at 355 nm will excite the porphyrin sub-unit preferentially.

In spite of the dominance of the porphyrin unit in the photophysics, two features indicate that the porphyrin moiety interacts with the $W(CO)_5$ moiety. First, the tungsten pentacarbonyl derivatives, especially of the zinc porphyrins, are prone to photodissociation of $W(CO)_5$ when irradiated in the 400–500 nm region where absorption by the porphyrin moiety dominates. Secondly, the fluorescence spectra of $W(CO)_5$**3b** and $W(CO)_5$**4b** exhibit an extra emission peak that arises from a photochemical process, perhaps electron transfer.

This research has also demonstrated that the MLCT excited states of $[W(CO)_5(py\text{-}CONH_2)]$ complexes overlap in energy with the LF excited states. The photochemistry of these complexes resembles that of unsubstituted $[W(CO)_5(py)]$.

Further work is underway to alter the structure of the porphyrin and/or the transition metal carbonyl unit in order to tune the properties of the resulting supermolecule to encourage stronger interactions between the two units.

Experimental

Spectroscopic methods

UV-Vis spectra were recorded on a Perkin-Elmer Lambda 7 spectrophotometer with a scan rate of 120 nm min^{-1} and a slit width of 2 nm. IR spectra were recorded on a Mattson RS FTIR instrument, averaging 16 scans at a resolution of 2 cm^{-1}. Solution samples for IR spectroscopy were prepared under argon. FAB (nitrobenzyl alcohol matrix), CI and EI mass spectra were recorded on a VG Autospec instrument. ES mass spectra were recorded on a Finnigan LCQ instrument. Mass spectra are quoted for ^{184}W and ^{64}Zn isotopes unless stated otherwise.

Fluorimetry measurements were recorded using a Shimadzu RF 1501 spectrofluorimeter or a Jobin Yvon-Spex Fluoromax-2 with right-angle illumination. The slits in both the excitation and emission monochromators were set to 2 nm except for solid state and weakly-emissive samples (5 nm). Solution samples were prepared under argon in a dry solvent in a fluorimetry cell equipped with a Young's tap such that the absorbance at the excitation wavelength was approximately 0.4. In most cases solutions were degassed by purging with Ar for a further 10 minutes before use but in the case of **5**, **6** or **7**, the fluorimetry samples were degassed by three freeze–pump–thaw cycles. All the porphyrin solutions used for emission had a concentration of *ca.* (1–3) × 10^{-5} mol dm^{-3} (more dilute solutions were required in order to obtain good excitation spectra), and the emission intensity varied from *ca.* 1.5 × 10^5 to 2.1 × 10^6 in the uncorrected spectra and from *ca.* 1.2 × 10^6 to 6 × 10^7 in the corrected spectra. Emission from the porphyrins is much more intense than emission from **5** which had uncorrected emission intensities of (2.5–6) × 10^4 at a concentration of *ca.* 7 × 10^{-5} mol dm^{-3}. UV-Vis spectra were recorded after fluorimetry to check that no decomposition had occurred. Solid state samples were prepared by filling a capillary with a solution of the sample and evacuating off the solvent to leave a thin coating of the solid. The capillary was then sealed. All fluorimetry data were processed using the programs "Isamain Datamax 2.2"[44a] and "Grams/386 3.01".[44b] Emission spectra were corrected for photomultiplier response by multiplying by the spectrometer correction factor, "mcorrect.spc",[44a] supplied by the manufacturer.

NMR spectra were run on a JEOL EX 270 (^{1}H at 270 MHz and ^{13}C at 67 MHz), an MSL 300 (^{1}H at 300.13 MHz and ^{13}C at 75.47 MHz), or a Bruker AMX 500 (^{1}H at 500.13 MHz and ^{13}C at 125.76 MHz) spectrometer. The spectra were referenced as follows: ^{1}H to residual protiated solvent at δ 7.15 (C_6D_6), δ 7.3 ($CDCl_3$), δ 7.1 ([$^2H_5$]pyridine), δ 3.7 ([$^2H_8$]THF), δ 2.0 (CD_3CN) and ^{13}C to solvent triplet at δ 77.0 ($CDCl_3$), triplet at δ 123.9 ([$^2H_5$]pyridine) and to the quintet at δ 68.6 ([$^2H_8$]THF). Most of the ^{1}H and ^{13}C NMR spectra were assigned using ^{1}H-^{1}H COSY spectroscopy and DEPT and ^{1}H-^{13}C HETCOR spectroscopy respectively. 2-D spectra were recorded on the AMX 500 spectrometer using a gradient probe.

Steady state photolysis

For the synthesis of [$W(CO)_5(THF)$], [$W(CO)_6$] solutions were irradiated with a 125 W medium pressure mercury arc lamp inside a cooling-water jacket connected to an Applied Photophysics Ltd 3110 240 V supply. The solution was placed around the mercury arc in a Pyrex photolysis sleeve (path length 2 mm, volume 20 cm^3), with Schlenk connections. Steady-state photolysis experiments were also carried out with a mercury arc lamp (Philips HPK 125 W), typically with both a cut-off filter and a water filter placed between the lamp and the sample. The sample was prepared in a dry solvent under argon and placed in either a UV-Vis cell with a Young's tap or in an IR cell under argon.

Laser flash photolysis with a 355 nm Nd-YAG laser

Samples were prepared in a flash cell, consisting of a 2 mm cuvette, degassing bulb and Young's PTFE tap, using a Schlenk line fitted with a diffusion pump. THF was added with a cannula such that the absorbance at 355 nm was between 0.7 and 1.0 and the solution concentration was (2–4) × 10^{-4} mol dm^{-3}. The cuvettes were then degassed by three freeze–pump–thaw cycles and back-filled with argon. UV-Vis spectra were recorded before and after the laser flash experiments to check that the samples had retained their chemical integrity.

The laser set-up is a modification of that reported previously[45,46] but with a 355 nm source obtained from a Q-switched QuantaRay3 Nd-YAG laser by frequency tripling of the 1064 nm output beam (pulse length *ca.* 10 ns, energy 8–10 mJ per pulse). The signal was detected with a monochromator, a red-sensitive Hamatsu R928 photomultiplier and Tektronix TDS520 digital oscilloscope. A 375 nm cut-off filter and/or a 355 nm dichroic filter were used when monitoring in the short wavelength region (*ca.* 400 to 550 nm). For longer wavelengths, a 550 nm cut-off filter was used, usually also with the 355 nm dichroic to remove second-order light scattering in the 710 nm region. Usually, transients were averaged for four, eight or sixteen shots with a repetition rate of 1 Hz. The samples were shaken before each set of shots to minimise localised effects of decomposition. The transient decays were obtained directly by setting the monochromator to a particular wavelength and excited state spectra were obtained by the point-by-point method. In-house programs were used to convert the voltage data into a form suitable for analysing using the software Microcal Origin 3.5.[44c] Transient absorption spectra were obtained from the decays measured at various wavelengths by taking an average ΔA value over 10 points for a particular delay time.

For time-resolved emission spectroscopy, the emission lifetime was very similar to the pulse length of the laser. The laser excitation pulse shape was therefore measured at 365 and 375 nm with a silica optical flat placed in the beam instead of a sample. In-house software was used to calculate a rise time for the excitation pulse (7 or 8 ns). For the sample data, a Gaussian rise time corresponding to the excitation pulse was deconvoluted from the exponential decay. For the free base porphyrins, fits were repeated until a minimum error in the decay lifetime was obtained. For the metalloporphyrins, deconvolution was not successful due to the shortness of the emission lifetimes. Time-resolved emission spectra were recorded point-by-point by taking the average voltage value from ten points on each trace, at the same delay for each wavelength. The delay was chosen such that the emission was maximised.

Materials

Commercial chemicals were from the following suppliers: tungsten hexacarbonyl from BDH, 3-formylpyridine, isonicotinamide, from Aldrich, H_2tpp from Avocado, zinc acetate from Fisons and isonicotinoyl chloride hydrochloride, nicotinamide and nicotinoyl chloride hydrochloride from Lancaster. For column chromatography either silica (silica gel 60, 70–230 mesh, Merck or ICN, or 230 to 400 mesh, Machery-Nagel), or activated alumina (Phase Separations), was used. TLC plates came from Merck (silica gel 60 F_{254}). Solvents and acids were obtained from Fischer. General solvents were used as obtained from the supplier. Solvents for Schlenk-line work were dried by refluxing over sodium dispersion + benzophenone (benzene, hexane, THF), or over phosphorus pentoxide (acetonitrile, chloroform, dichloromethane). After refluxing, the dried solvents were distilled and then stored under Ar in ampoules fitted with a Young's tap. Triethylamine (BDH) was dried over calcium hydride (Avocado), then stored over molecular sieves (grade 4 Å, BDH). $CDCl_3$ for NMR was either used as obtained from Fluorochem or obtained from Goss and dried over phosphorus pentoxide. CD_3CN and [$^2H_5$]pyridine were from Goss and C_6D_6 and [$^2H_8$]THF from Apollo. They were dried as follows: over calcium hydride and then over molecular sieves ([$^2H_5$]pyridine), over potassium (C_6D_6, [$^2H_8$]THF), over phosphorus pentoxide (CD_3CN). Dried NMR solvents were transferred into an NMR tube (Wilmad 528-PP fitted with a PTFE Young's tap), on a high-vacuum line with a vacuum of 4×10^{-4} mbar. THF for laser flash photolysis experiments was obtained from Sigma-Aldrich (99.9 + % HPLC grade) and dried by refluxing over calcium hydride under Ar for three days before distillation and collection under Ar. It was stored in an ampoule fitted with a Young's tap.

Syntheses

Principal spectroscopic data are provided in the tables and in the sections below. Additional data in different solvents may be found in the ESI. †

5-[4-(Nicotinamidyl)phenyl]-10,15,20-triphenylporphyrin 3a. Porphyrin **3a** was synthesised from porphyrin **2** on a Schlenk line by a modification of a literature procedure for an amide synthesis on a different aminoporphyrin.[47] 5-(4-Aminophenyl)-10,15,20-triphenylporphyrin (115 mg, 0.18 mmol), was dissolved in dry $CH_2Cl_2 : Et_3N$ (3 : 1) (20 mL) and 1.5 equivalents of (nic)Cl·HCl (nicotinoyl chloride hydrochloride), (49 mg, 0.28 mmol), were added. The solution was stirred and then refluxed under Ar for 10 min at ≈55 °C. The reaction was monitored by TLC using hexane : acetone (3 : 1). Once the reaction mixture had cooled, another 1.5 equivalents of (nic)Cl·HCl were added and the solution refluxed under Ar as before. The solvent was removed on the Schlenk line and the residue was redissolved in $CHCl_3$ and washed with water (2×30 mL), sodium hydrogen carbonate solution (2×30 mL), and water again (1×30 mL). It was then dried over magnesium sulfate, filtered and the solvent removed on a rotary evaporator. The solid was redissolved in a hexane : acetone (3 : 1) mixture and applied to a silica column (3.5×30 cm). The first band containing unreacted starting material was eluted with hexane : acetone (3 : 1) and the second band was eluted with hexane : acetone (2 : 1), then neat acetone. Alternatively, a silica column was used with $CH_2Cl_2 : CH_3CN$ (5 : 1) as the eluant. Under the latter conditions, the starting material and product had R_f values [TLC, $CH_2Cl_2 : CH_3CN$ (5 : 1)] of 0.89 and 0.44, respectively. The product was obtained as a purple solid (125 mg, 0.17 mmol, 93%). $\bar{\nu}_{max}$/cm^{-1} (Nujol) 1654 (amide CO). ESMS *m/z* 735.4 (MH$^+$, $C_{50}H_{35}N_6O$, 100%). HR-FAB for $C_{50}H_{34}N_6O$ calculated *m/z* 734.2794, observed *m/z* 734.2789. Difference = 0.5 mDa.

[Zinc 5-[4-(nicotinamidyl)phenyl]-10,15,10-triphenylporphyrin] 3b. Zinc acetate dihydrate (45 mg, 0.20 mmol) was added to the free base **3a** (77 mg, 0.10 mmol), in 150 mL of MeOH : $CHCl_3$ (1 : 1). The mixture was stirred for 30 min under N_2 at room temperature before being heated at 45 °C using a graphite bath. The reaction was monitored by TLC using $CHCl_3$: MeOH (9 : 1). After 90 min the reaction had reached completion and the reaction mixture was left to cool. The solvent was then removed on a rotary evaporator. The solid residue was redissolved in sufficient $CHCl_3$ to apply to a silica column (3.5×30 cm). The solution obtained was dichroic (purple and blue). The porphyrin was eluted from the column with $CHCl_3$: MeOH (19 : 1, then 9 : 1). The purple solid obtained was washed with hexane [TLC, R_f ($CHCl_3$: MeOH, 9 : 1) = 0.75] (77 mg, 0.097 mmol, 97%). Zinc pyridyl porphyrins aggregate in non-coordinating solvents.[48–50] Evidence for aggregation of this porphyrin was obtained *via* splitting of the Soret band and from the mass spectrum. The aggregates could be disrupted by addition of pyridine. $\bar{\nu}_{max}$/cm^{-1} (Nujol) 1695 (amide CO). ^{1}H NMR (300 MHz, [$^2H_5$]pyridine): δ 11.62 (1H, s, amide NH), 9.66 (1H, d, *J* 2.2 Hz, nicotinoyl), 9.20 (2H, d, *J* 4.5 Hz, β-pyrrole), 9.10 (2H, d, *J* 4.5 Hz, β-pyrrole), 9.06 (4H, s, β-pyrrole), 8.75 (1H, dd, *J* 4.8 Hz, *J* 1.8 Hz, nicotinoyl), 8.50 (1H, dt, *J* 7.8 Hz, *J* 1.8 Hz, nicotinoyl), 8.46 (2H, d, *J* 8.4 Hz, bridging phenyl), 8.35 (2H, d, *J* 8.4 Hz, bridging phenyl), 8.31 (6H, m, *ortho*-phenyl), 7.67 (9H, m, *meta*-/*para*-phenyl), 7.29 (1H, dd, *J* 7.8 Hz, *J* 4.8 Hz, nicotinoyl). ^{13}C{^{1}H} NMR (67 MHz, [$^2H_5$]pyridine, assigned using DEPT 67 MHz and ^{1}H-^{13}C COSY NMR 500 MHz): δ 166.1 (CO), 157.2 (CH, β-pyrrole), 153.0 (CH, nicotinoyl), 151.2 (C), 151.1 (C), 150.2 (CH, nicotinoyl), 144.3 (C), 140.0 (C), 139.9 (C), 136.2 (CH, nicotinoyl), 135.9 (CH, bridging phenyl), 135.4 (CH, *ortho*-phenyl), 132.8 (CH, β-pyrrole), 132.7 (CH, β-pyrrole), 132.5 (C), 128.2 (CH, *meta*-/*para*-phenyl), 127.3 (CH, *meta*-/*para*-phenyl), 124.0 (CH, nicotinoyl), 121.8 (C), 121.7 (C), 119.5 (CH, bridging phenyl). FAB-MS *m/z* 796.2 (M$^+$, $C_{50}H_{32}N_6OZn$, 100%). A cluster of peaks was also observed at *m/z* 1595 (<1%) due to the dimer of porphyrin **3b**. HR-FAB for $C_{50}H_{32}N_6O^{64}Zn$ *m/z* calculated 796.1929, observed *m/z* 796.1925. Difference = 0.4 mDa.

5-[4-(Isonicotinamidyl)phenyl]-10,15,20-triphenylporphyrin 4a. The free base **4a** was synthesised in the same way as its nicotinamidylphenylporphyrin isomer and was obtained in 86% yield [TLC, R_f ($CH_2Cl_2 : CH_3CN$, 5 : 1) = 0.41]. ESMS *m/z* = 735 (MH$^+$, $C_{50}H_{35}N_6O$, 100%). HR-FAB for $C_{50}H_{34}N_6O$ *m/z* calculated 734.2794, observed 734.2792. Difference = 0.2 mDa.

[Zinc 5-[4-(isonicotinamidyl)phenyl]-10,15,20-triphenylporphyrin] 4b. The zinc complex **4b** was synthesised in the same way as its nicotinamidylporphyrin isomer and was obtained in 91% yield [TLC, R_f ($CHCl_3$: MeOH, 9 : 1) = 0.54]. $\bar{\nu}_{max}$/cm^{-1} (Nujol) 1669 (amide CO). ESMS *m/z* 796.4 (M$^+$, $C_{50}H_{32}N_6OZn$, 100%). HR-FAB for $C_{50}H_{32}N_6O^{64}Zn$ *m/z* calculated 796.1929, observed *m/z* 796.1932. Difference = 0.3 mDa.

[W(CO)$_5$(4-CHO-py)] 5. Complex **5** was prepared by a modification of the literature procedure for the synthesis of [M(CO)$_5$(substituted pyridine)] complexes.[19,20] A dry THF solution (20 mL) of [W(CO)$_6$] (0.6 mmol) was irradiated with a UV-lamp for 5 h while bubbling N_2 through the solution. After 5 h the originally colourless solution had become yellow and an IR spectrum of the [W(CO)$_5$(THF)] complex was recorded to check that very little unreacted hexacarbonyl remained. The solution was then transferred *via* a cannula on an argon Schlenk-line into a Schlenk-tube wrapped in foil containing 4-CHO-py (0.6 mmol). The solvent was removed immediately by rotary evaporation to give a yellow/orange compound which was stored at 4 °C, under Ar and wrapped in foil. The product was further purified by washing with hexane. UV-Vis as lit.[19] Emission (methylcyclohexane, λ_{ex} 400 nm) λ_{max}/nm: 566 (uncorr., the signal was too weak to apply a correction factor). Lit. corrected value = 631 nm.[19] Emission (benzene, λ_{ex} 400 nm) λ_{max}/nm: 600 (uncorr.). Lit. corrected value = 650 nm.[19] Emission (solid state, λ_{ex} 400 nm) λ_{max}/nm: 580 (uncorr.). ^{1}H NMR (300 MHz, C_6D_6): δ_H 8.90 (1H, s, CHO), 7.97 (2H, d, *J* 6.60 Hz, isonicotinoyl), 6.19 (2H, d, *J* 6.60 Hz, isonicotinoyl).

[W(CO)$_5$(nicotinamide)] 6. Compound **6** was synthesised using a variation of the method above. The [W(CO)$_5$(THF)] solution (15 mL, 0.45 mmol) was added to the nicotinamide (55 mg, 0.45 mmol) in a Schlenk tube surrounded with aluminium foil. The solution was stirred for 1.5 h before the THF was removed by evaporation to obtain a yellow solid. Unwanted [W(CO)$_6$] was removed by washing six times with hexane, the product was dried under reduced pressure and stored at 4 °C under Ar (172 mg, 0.38 mmol, 85%). UV-Vis λ_{max}/nm (CH_3CN) 330 ($e^4b_2^2 \longrightarrow e^3b_2^2b_1^1$) and 374 (overlapping MLCT and $e^4b_2^2 \longrightarrow e^3b_2^2a_1^1$). λ_{max}/nm (CH_2Cl_2) 332 and 375.

λ_{max}/nm (THF, ε/dm^3 mol^{-1} cm^{-1}): 336 (5380) and 378 (5070). λ_{max}/nm (benzene) 339 (sh) and 386. Emission (solid state, λ_{ex} 400 nm) λ_{max}/nm: 548 (uncorr.). δ_H (300 MHz, [$^2H_8$]THF) 9.44 (1H, s, nicotinoyl), 9.18 (1H, d, *J* 5.5 Hz, nicotinoyl), 8.44 (1H, d, *J* 8.1 Hz, nicotinoyl), 7.61 (1H, dd, *J* 8.1 Hz, *J* 5.5 Hz, nicotinoyl), 7.72 (1H, br s, amide NH), 7.25 (1H, br s, amide NH). EIMS *m*/*z* 446 (M$^+$, $C_{11}H_6N_2O_6{}^{184}W$, 9%), 418 (M$^+$ − CO, 2), 390 (M$^+$ − 2CO, 14), 362 (M$^+$ − 3CO, 14), 334 (M$^+$ − 4CO, 18), 306 (M$^+$ − 5CO, 2), 122 (M$^+$ − W(CO)$_5$, 100), 106 (122 − NH$_2$, 63), 78 (106 − CO, 79).

[W(CO)$_5$(isonicotinamide)] 7. Compound **7** was synthesised and purified in the same way as compound **6**. It was obtained as a pale yellow solid in 87% yield (174 mg). UV-Vis λ_{max}/nm (CH$_3$CN) 379 (overlapping MLCT and $e^4b_2{}^2 \longrightarrow e^3b_2{}^2a_1{}^1$). λ_{max}/nm (CH$_2Cl_2$) 385. λ_{max}/nm (THF) 390. λ_{max}/nm (benzene) 398. Emission (solid state, λ_{ex} 400 nm) λ_{max}/nm: 550 (uncorr.). ^{1}H NMR (300 MHz, [$^2H_8$]THF): δ 9.19 (2H, d, *J* 5.2 Hz, isonicotinoyl), 7.85 (2H, d, *J* 5.2 Hz, isonicotinoyl), 7.76 (1H, br s, amide NH), 7.33 (1H, br s, amide NH). EIMS *m*/*z* 446 (M$^+$, $C_{11}H_6N_2O_6W$, 6%), 390 (M$^+$ − 2CO, 4), 362 (M$^+$ − 3CO, 3), 334 (M$^+$ − 4CO, 6), 306 (M$^+$ − 5CO, 2), 122 (M$^+$ − W(CO)$_5$, 43), 106 (122 − NH$_2$, 60), 42 (CH$_4$CN$^+$, solvent, 100).

[Tungsten pentacarbonyl {5-[4-(nicotinamidyl)phenyl]-10,15,20-triphenylporphyrin}] W(CO)$_5$3a. [W(CO)$_6$] (211 mg, 0.6 mmol) was dissolved in dry THF (20 mL) under Ar with the aid of a sonic bath and photolysed with a UV-lamp for 4.5 h. IR spectroscopy showed that most of the [W(CO)$_6$] had been converted to [W(CO)$_5$(THF)]. The free base porphyrin (21 mg, 0.029 mmol), was dissolved in 4 mL of dry THF in an ampoule equipped with a magnetic flea. To this [W(CO)$_5$(THF)] (1 mL, 1 equivalent) was added and the solution left stirring at room temperature. The reaction was monitored by IR spectroscopy. After stirring for 1 h, the IR band at 1890 cm^{-1} for the THF complex had shifted to 1899 cm^{-1} indicating the formation of W(CO)$_5$**3a**. The mixture was left stirring for a further 15 h. The solution, which was purple initially, became brown. The solvent was then removed by evaporation and the product was purified by dissolving it in benzene, layering with hexane and leaving at 4 °C overnight. W(CO)$_5$**3a** precipitated out of solution and the solvent, containing any unreacted [W(CO)$_6$], was filtered off. The product was stored at 4 °C under Ar (28 mg, 0.026 mmol, 91%). ESMS *m*/*z* 1058.4 (M$^+$, $C_{55}H_{34}N_6O_6W$, 73%), 735.5 [M$^+$ − W(CO)$_5$, 100].

[Tungsten pentacarbonyl {zinc 5-[4-(nicotinamidyl)phenyl]-10,15,20-triphenylporphyrin}] W(CO)$_5$3b. W(CO)$_5$**3b** was synthesised using the same method as for W(CO)$_5$**3a**. The zinc porphyrin (24 mg, 0.030 mmol) was dissolved in dry THF (4 mL) in an ampoule equipped with a magnetic flea and surrounded in foil. To this [W(CO)$_5$(THF)] (0.030 mmol) was added and the solution left stirring at room temperature overnight during which time the solution turned from purple to brown. On one occasion the reaction was followed by IR spectroscopy; which revealed that the reaction with **3b** was much slower than with **3a**, probably because of the poor solubility of **3b** in THF. Recrystallisation was carried out as for W(CO)$_5$**3a** (30 mg, 0.027 mmol, 89%). ESMS *m*/*z* 1122.3 (M$^+$, $C_{55}H_{32}N_6O_6{}^{186}W^{64}Zn$ and $C_{55}H_{32}N_6O_6{}^{184}W^{66}Zn$, 20%), 796.4 [M$^+$ − W(CO)$_5$, 100].

[Tungsten pentacarbonyl {5-[4-(isonicotinamidyl)phenyl]-10,15,20-triphenylporphyrin}] W(CO)$_5$4a. W(CO)$_5$**4a** was synthesised by the same method as for W(CO)$_5$**3a**. Yield 85%. ESMS *m*/*z* 1059 (MH$^+$, $C_{55}H_{35}N_6O_6W$, 100%), 735 [M$^+$ − W(CO)$_5$, 61].

[Tungsten pentacarbonyl {zinc 5-[4-(isonicotinamidyl)phenyl]-10,15,20-triphenylporphyrin}] W(CO)$_5$4b. W(CO)$_5$**4b** was synthesised and purified using the same method as for W(CO)$_5$**3a**. Yield 84%. ESMS *m*/*z* 1122 (M$^+$, $C_{55}H_{32}N_6O_6{}^{186}W^{64}Zn$ and $C_{55}H_{32}N_6O_6{}^{184}W^{66}Zn$, 100%), 796 [M$^+$ − W(CO)$_5$, 67].

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