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Phthalocyanine Sensitized Reduction of Methyl Viologen using Visible Light

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A detailed study is reported of the ability of a range of metallophthalocyanines to photoreduce methylviologen, in the presence of triethanolamine. Certain species are demonstrated to be effective photocatalysts, using light of wavelength corresponding to the Q band in their electronic spectrum. However quantum yields are very low. Other metallophthalocyanines are shown to be inactive under similar conditions. Using electrochemical and spectroscopic data the energies of the photoactive states are estimated. From these results the thermodynamic driving forces for both oxidative and reductive quenching are calculated, together with the thermal following and back reactions. By comparison with other photoactive systems, with known kinetic data, it is demonstrated that the thermodynamic data are a useful guide to photoactivity when kinetic data are unavailable.

Introduction

In recent years various porphyrins and phthalocyanines have been used to photocatalyse the reduction of water to hydrogen, either directly, or via a relay such as methyl viologen [1–11]. In general quantum yields have proven to be small.

Phthalocyanines and porphyrins are attractive candidates for the design of photocatalysts since they are highly coloured, exhibit varied redox activity and are generally, chemically stable. Phthalocyanines appear to have especial advantages in that they are more intensely coloured at the red end of the visible spectrum (λ_{max} 600–725 nm) and are more resistant to ring degradation than are the porphyrins [12].

Moreover the lifetimes of the excited spin triplet transitions, where identified are in the microsecond to millisecond range, certainly long enough for significant bi-molecular quenching [13]. In this paper we discuss the photocatalytic activity of a series of main group and transition metal phthalocyanines (MPc) towards the photoreduction of methyl viologen, and explain the results in terms of the redox energy levels of the molecules concerned.

The photocatalytic activity is generally low, but these studies establish ground rules for the design of more successful reagents. Comparison with some porphyrin data is also included. Ferraudi [14] has previously reported the UV photochemistry of some tetrasulphonated metallophthalocyanines.

Experimental

Unsubstituted metallophthalocyanines [12] and tetrasulphonated phthalocyanine metal complexes, TsPcM (M = Cr, Fe, Co, Ni, Cu) [15] were prepared following literature procedures. The former were purified by sublimation under high vacuum and the latter by chromatography through cellulose (eluent, water).

Tetra-t-butyl substituted metallophthalocyanines, TbPcM (M = TiO, VO, Ni(II), Zn(II), ClRh(III)) were also prepared according to literature methods [16]. Carbonyl(4-t-butylpyridine)phthalocyaninatoruthenium(II) was prepared according to Dolphin and James [17]. Tetra(octylsulphonamido)phthalocyanatochromium(III) hydroxide (ToPcCr(III)OH) and tetra(dodecylsulphonamido)phthalocyanatoiron(II) (TdPcFe(II)) were prepared by the following general reaction.

Thionyl chloride (*ca.* 50 ml) was distilled, under nitrogen, onto the sodium salt of TsPcM(III) (M = Cr, Fe) and the mixture refluxed for eight hours. Subsequently the green solid obtained is washed with dry toluene, to remove excess thionyl chloride and then refluxed overnight, under nitrogen, with dodecylamine (10 g, Aldrich) (or octylamine, 10 g). The product is very soluble in most organic solvents. Both chromium and iron derivatives were purified by chromatography through neutral alumina (eluant, chloroform). Note that the amine affects reduction of the iron(III) leading to an iron(II) product. In an alternative procedure, the thionyl chloride is pumped off the initial reaction mixture, after completion of the reaction, and the amine added directly thereto.

ToPcCr(III)OH electronic spectrum in THF (λ_{max}, nm; (log ε)), 680(4.55) , 643(4.07), 611(4.00), 692(3.45), 340(4.22). *Anal.*: Calc. for $C_{64}H_{85}CrN_{12}$-

O_9S_4 C, 57.1; H, 6.4; N, 12.5%. Found: C, 57.5; H, 6.8; N, 12.8%.

TdPcFe(II) electronic spectrum in THF (λ_{max}, nm; (log ϵ)), 675(5.00), 612(4.68), 454(4.57), 358 (5.01). *Anal.*: Calc. for $C_{80}H_{116}FeN_{12}O_8S_4$ C, 61.7; H, 7.5; N, 10.8%. Found: C, 61.6; H, 8.0; N, 10.8%.

The purities of most of the soluble metallophthalocyanines were ensured by analytical HPLC (Spectrophysics model 8500) on silica columns. Water was glass distilled from potassium permanganate. All solvents were Spectrograde and used without further purification. Triethanolamine (TEOA) and methylviologen (Paraquat CARE! very toxic by oral or skin absorption) were used as supplied (Aldrich).

Electronic spectra were recorded on a Hitachi-Perkin Elmer model 340 microprocessor UV/VIS/NIR spectrometer.

Electrochemical data were recorded with Princeton Applied Research models 173, 174a, 175, and 179, a Houston 9002A XY recorder and a Tektronix 5103N storage oscilloscope using cyclic voltammetry. A platinum wire was used as working electrode referenced to an sce. Full details have been presented elsewhere [18].

Quenching studies were carried out using a Varian SF 330 spectrofluorimeter.

Irradiations employed a 250w quartz halogen lamp in conjunction with a UV cut-off (350 nm) or blue cut-off (640 nm) broad band filter or a narrow band (10 nm) filter appropriate to the Q band of the photocatalyst employed. The intensity of the light was monitored with an Alphametrics Model DC 1010 radiometer. All solutions were prepared immediately before measurement, degassed through several freeze-thaw cycles and maintained at constant temperature (296 K) with a thermostatted water bath. Appropriate blank experiments were *always* carried out in the absence of added photocatalyst to ensure its efficacy.

Results

A range of metal phthalocyanines, specifically those of OTi(IV), OV(IV), M(II) where M = Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ru and M(III), M = Cr, Mn, Rh were screened for photocatalytic activity.

In the initial experiments a degassed mixture of metallophthalocyanine, triethanolamine (TEOA), and methyl viologen (MV^{2+}) in THF/water (15:85) was irradiated with visible light ($\lambda_{max} > 350$ nm). When reduction of methyl viologen occurs, the characteristic spectrum of MV^+ appears (λ_{max} 395, 605 nm [19]).

The reduction of methyl viologen may occur through two alternative routes (or both at the same time), namely, oxidative quenching:

$$\mathrm{MPc} \xrightarrow{h\nu} \mathrm{MPc}^* \tag{1}$$

$$Q_{ox}: \quad \mathrm{MPc}^* + \mathrm{MV}^{2+} \rightarrow \mathrm{MPc}^+ + \mathrm{MV}^+ \tag{2}$$

$$Th_{ox}: \quad \mathrm{MPc}^+ + \mathrm{TEOA} \rightarrow \mathrm{MPc} + \mathrm{TEOA}^+ \tag{3}$$

or reductive quenching:

$$\mathrm{MPc} \xrightarrow{h\nu} \mathrm{MPc}^* \tag{1}$$

$$Q_{red}: \quad \mathrm{MPc}^* + \mathrm{TEOA} \rightarrow \mathrm{MPc}^- + \mathrm{TEOA}^+ \tag{4}$$

$$Th_{red}: \quad \mathrm{MPc}^- + \mathrm{MV}^{2+} \rightarrow \mathrm{MPc} + \mathrm{MV}^+ \tag{5}$$

The reactions (2) and (4) will generally return to reactants, unless there is a kinetic reason for suppressing these back reactions (6) and (7):

$$Bac_{ox}: \quad \mathrm{MV}^+ + \mathrm{MPc}^+ \rightarrow \mathrm{MV}^{2+} + \mathrm{MPc} \tag{6}$$

$$Bac_{red}: \quad \mathrm{TEOA}^+ + \mathrm{MPc}^- \rightarrow \mathrm{TEOA} + \mathrm{MPc} \tag{7}$$

A destructive reaction between the products $TEOA^+$ and MV^+ is not considered because $TEOA^+$ rapidly decomposes.

A specific route may be facilitated by changing the concentration of TEOA and/or MV^{2+} *i.e.* by driving the reaction in a Nernstian sense. Various ratios of reagents were therefore investigated. In Table I we summarise the initial results of this survey.

After investigation with a range of ratios of reactants, with solutions buffered at various pH, and using white light above 350 nm, (see Table I) only certain derivatives of Mg(II), Zn(II), Cr(II), Mn(II), Fe(II), Ru(II) and Rh(III) proved effective in generation of net reduced methylviologen. Using filters which cut off light of wavelength shorter than 640 nm it was readily demonstrated that irradiation into the Q band was the photoactive process. In certain cases (see Table I) narrow band filters were used, irradiating directly into the Q band.

A positive result indicates unequivocal net generation of reduced methyl viologen within a reasonable time period (less than 15 min irradiation). The quantum yields are of the order of 10^{-3}. As shown in Table I certain of the trivalent complexes, such as Fe(III), were photoreduced to M(II). This photoreduction to M(II) may be a photoassisted downhill reaction.

No net formation of reduced methylviologen was observed for any trivalent species except for rhodium(III).

In general the transition metal phthalocyanine sulphonic acid species, M(II)TsPc were inactive

TABLE I. Photoreduction irradiation Experiments.

Complex^a	Q band (log ε)	Light	Solvent	Result^b
PcMg(Py)$_2$	662	>500 nm	THF/water	MV$^+$
TbPcTiO	693(5.19)	white	THF/water	MV$^+$
TbPcVO	675	white	THF/water	x
ToPcCr(III)	680	>640 nm	THF/water	Cr(II)
ToPcCr(II)^c	612	600 nm	THF/water	MV$^+$ (Φ 2.6 × 10^{-3})
TbPcMn(III)	716(5.13)	white	THF/water	Mn(II)
TsPcFe(III)	626(4.36)	white	water, pH 4	x
			pH 7	x
			pH 10	Fe(II)
TdPcFe(II)	675(5.00)	650 nm	THF/water	MV$^+$
TsPcCo(II)	663(5.11)	white	water, pH 7	x
TbPcNi(II)	677(5.34)	white	THF/water	x
TsPcCu(II)	677(5.44)	white	water, pH 7	x
TbPcZn(II)	684(5.40)	>640 nm	THF/water	MV$^+$
TbPcRh(III)Cl	650(5.06)	>640 nm	THF/water	MV$^+$
PcRu(II)CO	640	white	THF/water	MV$^+$

^{a}TbPc = tetrabutylphthalocyanine; TsPc = tetrasulphonatophthalocyanine; TdPc = tetradodecylsulphonamidophthalocyanine; ToPc = tetraoctylsulphonamidophthalocyanine. ^{b}Yields, unless indicated are approximately 10^{-3}. ^{c}Prepared from the chromium(III) complex by *in situ* irradiation in the presence of cysteine. See experimental section for details of the irradiation experiments.

towards reduction of methylviologen, but their alkylsulphonamido derivatives were active as shown in Table I.

Discussion

The following factors are important in assessing the efficiency of methylviologen reduction in experiments involving continuous irradiation of solutions of photocatalyst, TEOA and MV^{2+} [20–22].

1. Quantum yield for population of the photoactive excited state.

2. Relative lifetime of the excited state, *i.e.* is it long lived enough for significant bimolecular quenching.

3. Rate of uni-molecular back electron transfer within the cage *versus* diffusion of products out of the cage.

4. Relative rate of bi-molecular back electron transfer.

Few of these species luminesce so that direct observation of quenching by acceptors (oxidative) or donors (reductive) cannot generally be carried out. Where luminescence is observed, the photoactive state phosphoresces near 1000 nm [13] a difficult region for study. We anticipate obtaining such data in the future.

Nevertheless we do possess detailed information of the redox potentials of these species and upon their detailed electronic spectra [18, 23–25]. These data may be used to predict, qualitatively, the redox energy of the lowest (spin forbidden) excited state which is expected to be the photoactive level. Although a detailed knowledge of kinetic processes is important for a complete understanding of the photochemistry of these species, the general data presented in Table I allow thermodynamic data to be used in a constructive manner.

The thermodynamic driving force of the reactions in eqns. 2–5 can be calculated if the energy of the relevant photoactive state is known. Such information is best obtained using quenching data from a range of quenchers of varying redox energy [26–28]. However it can also be estimated from ground state redox potentials and absorption or preferably emission spectra. This method is inaccurate by an amount equal to the vibrational excitation, if the (0–0) emission cannot be observed. However the spin singlet transitions in MPc chemistry are often (0–0) in nature, giving cause to believe that the spin triplets may be the same. The estimate should indeed be fairly accurate.

In Table II we report ground state redox data for the couples of interest under solvent conditions similar to those used for the photochemistry. Table II also reports the energy (or maximum) energy of the lowest, and presumably, photoactive state.

This lowest state may arise in several possible ways: *i*) in closed shell species it is the spin triplet

TABLE II. Observed Low Energy Absorption, Ground State Potentials and Excitation Energies (*versus* NHE).[a]

Name	Obs. Trans.	Exen	c^+/c	c/c^-
PcMg	14.8 (Q)	1.2	0.94	−0.71
TbPcTiO	14.4 (Q)	1.2	1.25	−0.25
TbPcVO	NIR (d–d)	0.5	1.26	−0.24
ToPcCr(II)	11.8 (LMCT)	0.8	$-0.15^{\#}$	−0.75
ToPcCr(III)	7.9 (LMCT)	0.4	1.25	$-0.15^{\#}$
TbPcMn(II)	10.9 (LMCT)	0.7	$0.11^{\#}$	−0.45
TbPcMn(III)	7.6 (LMCT)	0.3	1.13	$0.11^{\#}$
TdPcFe(II)	15.0 (Q)	1.2	$0.45^{\#}$	$-0.45^{\#}$
TsPcFe(III)	(4) (LMCT)	0	1.13	$0.65^{\#}$
TsPcCo(II)	NIR (d–d)	0.5	$0.65^{\#}$	$0.05^{\#}$
TbPcNi(II)	14.9 (Q)	1.2	1.3	−0.65
TsPcCu(II)	9.25 (QD)	1.15	1.25	−0.59
TbPcZn(II)	14.6 (Q)	1.15	0.95	−0.64
TbPcRh(III)	15.2 (Q)	1.15	1.00	−0.43
PcRu(II)(CO)	15.6 (Q)	1.15	1.15	−0.45

[a] Transition energies in kilokaysers, potentials in volts. Electrochemical data are for DMF solution using tetraethylammonium perchlorate as supporting electrolyte [23–25, and this work]. # Signifies redox couple on the metal, otherwise the redox process occurs on the phthalocyanine ring. Q = Q band; (QD = doublet–quartet; d–d = d–d transition; LMCT = ligand to metal charge transfer.

component of the Q(π–π*) band designated ^{3}Q. Phosphorescence from this state has been observed in the range 850–1000 nm for several metallophthalocyanines [13], *i.e.* about 5500 cm^{-1} below the Q band absorption. ^{3}Q is the lowest band for the titanyl, low spin iron(II), nickel, zinc, magnesium, rhodium(III) and ruthenium(II) species discussed here. *ii*) the band may be charge transfer in origin, either ligand (Pc) to metal (LMCT) or metal to ligand (Pc), (MLCT). A detailed analysis of the charge transfer states of metallophthalocyanines has recently been completed [29]. PcMn(III) and PcCr(III) both exhibit very low energy charge transfer LMCT bands (in absorption) from as low as 8000 cm^{-1}, assigned as $^1E_u \leftarrow {}^1A_{1g}$ ($a_{1u} \rightarrow e_g$) transitions. These are very narrow, apparently (0–0) in nature.

The corresponding LMCT bands in the Mn(II) and Cr(II) complexes are blue shifted and appear near 850 nm (1.5 eV) [29]. By analogy with the Q band, the spin triplet components of these LMCT transitions probably lie about 5500 cm^{-1} to lower energy [13].

The Fe(III) complex has a hole in the t_{2g} (in O_h) orbital set. Calculation [29] suggests an LMCT band may be as low as 4000 cm^{-1} but it has not been observed. We consider the possible presence of MLCT transitions below. *iii*) d–d transitions may occur at low energies. The Co(II) complex is probably five coordinate in THF/water and will exhibit low energy d–d absorption [30–33]. The vanadyl complex will possess one electron in the split components of t_{2g} (in O_h) and will also have very low energy d–d transitions. *iv*) 'Trip–multiplet' transitions can be generated by the coupling of spin states on the metal with the ^{3}Q state on the phthalocyanine. The Cu(II) complex exhibits a low lying doublet–quartet transition due to this mechanism [13, 29, 34].

Allowing for the spin triplet state to lie about 5000 cm^{-1} below the singlet provides the Exen data shown in Table II. The thermodynamic driving forces for oxidative (2) and reductive (4) quenching, the following thermal reactions (3) and (5), and the back reactions (6) and (7) can be estimated and are shown in Table III (see Appendix).

Before discussing these data recall that the energies listed in Table III refer to standard conditions wherein all reagents are at unit activity. This is certainly not the case experimentally. The experimental conditions, (typically, *e.g.* 10^{-2} MV^{2+} and 10^{-4} to10^{-5} MV^{+}) provide a Nernstian driving force of some 0.1–0.2 V which can be added, where appropriate, to the data in Table III. Moreover the irreversible nature of the oxidation of TEOA [35] may lead to an additional driving force for reductive quenching of some 0.3–0.4 V.

It seems appropriate to look at certain of the fairly successful systems in the literature, where corresponding kinetic and thermodynamic information is available, and see how these results compare with the thermodynamic data reported here.

Such data are reported for moderately successful systems involving ruthenium bipyridyl and bipyrazyl, proflavin, a zinc porphyrin (zinc tetramethylpyridinium porphyrin, $TmPyPZn^{4+}$) and a zinc phthalocyanine ($TsPcZn^{4-}$) derivative, for experimental conditions similar to those used here, in Table IV.

These systems all show either a positive Q_{ox} or positive Q_{red} except for $ZnTsPc^{4-}$. The quantum yields for MV^+ formation are highest for the Ru(bipyrazyl)$_3^{2+}$ system [36] and Proflavin system [37] which have high Q_{red}, and for Ru(bipyridyl)$_3^{2+}$ [36] with large Q_{ox}. Quantum yields are not reported* for $ZnTmPyP^{4+}$ [38] and $ZnTsPc^{4-}$; however it is known that the efficiency of $ZnTmPyP^{4+}$ (Q_{ox} = 0.36 V) is much higher than the very inefficient $ZnTsPc^{4-}$, for which both Q_{ox} and Q_{red} are negative (under standard conditions). While kinetic problems associated with factor (3) above are likely to be important in the anionic $ZnTsPc^{4-}$, (see for example [9]), it is interesting that the low quantum yield is reflected in the negative thermodynamic Q_{ox} and Q_{red} for $ZnTsPc^{4-}$.

The fate of the excited state is readily inferred where quenching studies are available. For example, in the Ru(bipyridyl)$_3^{2+}$ system, it is seen that the

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*See Note added in proof, ref. [50].

TABLE III. Calculated Excited State Redox Energies, Ground State and Excited State Driving Energies and Back Reaction Driving Energies.[a]

	c^+/c^*	c^*/c^-	Q_{ox}	Th_{ox}	Q_{red}	Th_{red}	Bac_{red}	Bac_{ox}
PcMg	−0.25	0.49	−0.19	0.12	−0.33	0.27	1.53	1.38
TbPcTiO	0.05	0.95	−0.5	0.43	0.13	−0.2	1.07	1.7
TbPcVO	0.76	0.26	−1.21	0.44	−0.56	−0.21	1.06	1.71
ToPcCr(II)	−0.95	0.05	0.5	−0.97	−0.77	0.3	1.57	0.3
ToPcCr(III)	0.85	0.25	−1.3	0.43	−0.57	−0.3	0.97	1.7
TbPcMn(II)	−0.59	0.25	0.14	−0.71	−0.57	0	1.27	0.56
TbPcMn(III)	0.83	0.41	−1.28	0.31	−0.41	−0.56	0.71	1.58
TdPcFe(II)	−0.75	0.75	0.3	−0.37	−0.07	0	1.27	0.9
TsPcFe(III)	1.13	0.65	−1.58	0.31	−0.17	−1.1	0.17	1.58
TsPcCo(II)	0.15	0.55	−0.6	−0.17	−0.27	−0.5	0.77	1.1
TbPcNi(II)	0.1	0.55	−0.55	0.48	−0.27	0.2	1.47	1.75
TsPcCu(II)	0.1	0.56	−0.55	0.43	−0.26	0.1	1.41	1.7
TbPcZn(II)	−0.2	0.51	−0.25	0.13	−0.31	0.19	1.46	1.4
TbPcRh(III)	−0.2	0.77	−0.25	0.18	−0.05	−0.02	1.25	1.45
PcRu(II)(CO)	−0.05	0.75	−0.40	0.33	−0.07	0	1.27	1.6

[a]For significance of column headings see text, equations (1) through (7), and Appendix. See footnotes to Table I.

TABLE IV. Calculated Excited State Redox Energies, Ground State and Excited State Driving Energies and Back Reaction Driving Energies for Some Literature Photocatalysts.

	$Ru(bipy)_3^{2+}$	$Ru(BPZ)_3^{2+}$	Proflavin	$ZnTmPyP^{4+}$	$ZnTsPc^{4-}$
Ref.[a]	[45]	[36]	[46]	[9]	[7]
Ex energy	2.1	2.1	2.18	1.8	1.2
c^+/c	1.26	1.73		1.2	0.95
c/c^-	−1.26	−0.79	−0.78	−1.0	−0.65
c^+/c^*	−0.81	−0.37		−0.6	−0.25
c^*/c^-	0.77	1.31	1.40	0.8	0.55
Q_{ox}	0.39	−0.08		0.1	−0.2
Th_{ox}	0.44	0.91		0.38	0.13
Q_{red}	−0.05	0.49	0.58	−0.02	−0.27
Th_{red}	0.81	0.34	0.33	0.55	−0.2
Bac_{ox}	1.71	2.18		1.65	1.40
Bac_{red}	2.08	1.6	1.60	1.82	1.47
$k(MV^{2+})$ $(m^{-1}\ s^{-1})$	2.4×10^{9b}			2×10^6	7×10^6
τ(ms)	0.00068	0.001	0.2–0.4[c]	1.3	0.245
ΦMV^+	0.019[d]	0.77[e]	0.6[f]	0.75[g]	

See Footnotes of Tables II and III. [a]These references refer to source of ground and excited state potentials, kinetic parameters *etc.* except where otherwise indicated. [b]Refs. [28, 47]. [c]Refs. [48, 49]. [d]0.6 *M* TEOA, 0.02 *M* MV^{2+}, 6×10^{-5} *M* catalyst, λ 435 nm [36]. [e]0.2 *M* TEOA, 0.06 *M* MV^{2+}, 5.75×10^{-5} *M* catalyst, λ 435 nm [36]. [f]0.1 *M* EDTA, 0.01 *M* MV^{2+} 10^{-5} *M* catalyst, pH 6.5, Ref. [37]. [g]Ref. 50.

excited state lifetime is sufficiently long (680 ns) to allow efficient quenching by MV^{2+} (at $[MV^{2+}] = 10^{-2}$ *M*, $t_{1/2}$ for quenching is 29 ns) under typical experimental conditions. Gratzel reports [39] no observable quenching by TEOA at 0.4 *M* TEOA and Whitten's quenching rate [28] for an analogous but probably faster donor, Me_2NPh, k = 7.2 × 10^7 m^{-1} s^{-1} shows that with this donor, reductive quenching would only compete with oxidative at $[Me_2NPh]/[MV^{2+}]$ ratios exceeding 30. Thus the reported quantum yield of 19% [36] for Ru(bipyridyl)$_3^{2+}$ at $[MV^{2+}] = 0.06$ *M* and [TEOA] = 0.2 *M* must be due to oxidative quenching.

Returning to Table IV we note that both Q_{ox} and Q_{red} are positive for Ru(bipyridyl)$_3^{2+}$, but the more thermodynamically favoured Q_{ox} is the path used. Whilst the rates need not necessarily parallel Q_{ox} and Q_{red}, it is generally observed that quenching rate constants parallel thermodynamic driving force where a similar series of quenchers is used (as is expected from Marcus' theory [28]). The Ru(bipyrazyl)$_3^{2+}$ and Proflavin systems proceed *via* reductive quenching [36, 37] and Q_{ox} is negative whilst Q_{red} is +0.49 V. It seems that the quenching route can, with care, be inferred from thermodynamic considerations; clearly, however, detailed quenching studies must be used to firmly establish the pathway. With this caveat in mind, the data for the phthalocyanine systems in Tables I–III may be assessed.

Positive driving forces for quenching only occur for chromium(II), manganese(II), and iron(II) species *via* oxidative quenching, and for titanyl *via* reductive quenching, (see Tables II and III). Considering addition of 0.1–0.2 V for the non-standard state, the chlororhodium(III), carbonyl(4-t-butylpyridine)-ruthenium(II) and iron(II) species become downhill *via* reductive quenching and magnesium *via* oxidative quenching [40]. We note in passing that the quantum yield for loss of carbon monoxide [41] in the ruthenium complex is several orders of magnitude less than its photoredox activity, under the solvent conditions employed, so that it is an effective catalyst over a reasonable period of time.

It is surely significant that it is exactly these species which do exhibit net photoreduction of methylviologen, and that no others other than zinc are photoactive.

In addition to considering Q_{ox} and Q_{red}, it is also necessary to evaluate the parameters for the thermal following reactions. In the case of oxidative quenching the reaction Th_{ox} (3) must compete with Bac_{ox} (6) in order for net reduced methyl viologen production to be observed (for reductive quenching Th_{red} (5) must compete with Bac_{red} (7)). The significance of the thermodynamic quantities Th_{ox} and Bac_{ox} may be understood in the Ru(bipyridyl)$_3^{2+}$ system where kinetic data are also known. Thus despite Bac_{ox} being 1.3 V more favourable than Th_{ox} (1.7 V *versus* 0.4 V) the kinetic data for this system show [39, 42] that under the conditions of the quantum yield measurement (10^{-5} MV^+ and 10^{-1} TEOA [36]) the Th_{ox} reaction will dominate over Bac_{ox}.

In the phthalocyanine complexes of Cr(II), Mn(II), and Fe(II) the Th_{ox} reaction seems to be prohibitively unfavourable. This may account for the much lower yields in these systems compared with Ru(bipyridyl)$_3^{2+}$ [36]. For the reductive quenching rates, Th_{red} is considerably more favourable and the systems may proceed *via* this route for this reason in spite of less favourable Q_{red} values. Note that the pursuance of one pathway does not exclude use of the other. Both may occur, though usually one will predominate.

TdPcFe(II) is fluorescent with emission quenched by TEOA (reductive) but not by MV^{2+}, though this does not prove that the photoactive state is reductively quenched. It is interesting to speculate that the important route for methylviologen reduction for ToPcCr(II) and TbPcMn(II) whose photoactive states are probably LMCT in nature, is oxidative quenching whilst for TdPcFe(II), TbPcTiO, PcRu(II)CO(4-t-butylpyridine), TbPcRh(III)Cl, and PcZn (and PcMg whose Th_{red} is very favourable) all of whose photoactive states are probably π–π^* it is reductive quenching. Experimental data to prove this contention are being sought.

Darwent noted [1] that TsPcZn is photoactive *via* reductive quenching, though with very small efficiency (smaller than the TbPcZn reported here). Our thermodynamic data are consistent if about 0.3 V driving force is added. The successive reaction, Th_{red}, is downhill, which will serve to drive the reaction. TbPcNi(II), with similar thermodynamic parameters is inactive. However because of the differences in conditions of the electrochemical and photochemical experiments, the data reported in Tables II and III must not be treated too rigorously.

The charge on the species is also important. The tetrasulfonic acid species of Cr(II) and Fe(II) (in slightly acid pH) carrying up to four negative charges are inactive in the reduction of methyl viologen under the conditions employed. Long chain sulfonamido derivatives with four, eight, twelve or sixteen carbon atoms are active to much the same degree. In the case of zinc phthalocyanine where reductive quenching apparently occurs [1] both PcZn(II) and TsPcZn(II) are effective though to different degrees. The reduced quantum yield for negatively charged species presumably arises from back electron transfer within the cage (factor *3* above) as had previously been discussed for $ZnTmPyP^{4+}$ and $ZnTsP^{4-}$ species [9]. In the anionic complexes the strongly bound catalyst–methyl viologen ion pair does not separate, facilitating the back reaction.

We have been unable to confirm an earlier report [4] of very high efficiencies for methylviologen reduction using PcMg, PcCd, *etc.* We anticipate very low yields and indeed, using the conditions of these workers, we found only very low yields.

The Cr(II) and Mn(II) complexes are readily oxidised. Low lying MLCT transitions should occur. These have not been observed but should lie to the red of the LMCT transitions [29]. Their presence would seem to vitiate the calculation in Table III for these ions by providing a pathway to waste all the energy. Experimentally this appears not to be the case. The reason lies in consideration of intersystem crossing rates. Irradiation of the Q band places about 1.8 eV of energy into the molecule. This energy can cascade into the LMCT states which possess the same symmetry and differ by no more than one spinor orbital from a Q state. The intersystem crossing rate must be in the nanosecond regime since frequently both fluorescence (lifetimes of the order of a few nanoseconds) and phosphorescence (lifetimes of the order of microseconds) [13], can be observed.

The MLCT states differ by two spinor orbitals from the LMCT states, and intersystem crossing must surely be much slower; (intersystem crossing depends upon one electron operators) [43] time is therefore provided for the LMCT state to undergo photoreaction before it degrades to the MLCT state. 'Sticky' excited states where intersystem crossing is inhibited by selection rules have been discussed [44]. Indeed non-radiative intersystem crossing from the Q π–π^* state into an LMCT state is likely to be 'sticky' [44] suggesting that redox chemistry may be observed from both the spin triplet Q excited state and the spin triplet LMCT state.

Finally it is worth noting an inherent limitation of photocatalysts which harvest the red end of the visible spectrum. As a result of the lower energy of red light, the excitation energy (Exen) is about 0.5 V less energetic than available in $\mathrm{Ru(bipy)_3^{2+}}$, $\mathrm{Ru(bipyrazyl)_2^{3+}}$, proflavin and many of the porphyrins. This lower Exen quite naturally leads to more negative Q_{ox} and Q_{red}.

In the $\mathrm{MV^{2+}}$/TEOA system we seek to store 1.27 V (standard state). This is clearly not possible in a single photon process using red light. Even with the more efficient photocatalysts which use light of wavelength 400–500 nm a significant part of the net energy stored derives from the thermodynamic driving force arising from the irreversible decomposition of $\mathrm{TEOA^+}$.

This work shows that thermodynamic data can be extremely useful in the selection of promising photocatalysts from a homologous series such as the metallophthalocyanines. Those systems with favourable Q_{ox} or Q_{red} give net photoreactivity. In using these systems to harvest the red end of the visible region, it will be necessary to be content with storage of less than 1.2 V if greater efficiency is to be obtained. This may be accomplished by a judicious choice of redox potentials for the donor and acceptors used. However, as in photosynthesis, it is also possible that phthalocyanines can be used in a red absorbing system capable of upconversion with two or more photons.

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Appendix

Equations used to generate data in Tables II–IV (all data in volts).

i) Exen = (ν – 5000)/8065 (ν in wavenumbers)
ii) c^+/c = energy of first oxidation couple, *vs.* nhe.
iii) c/c^- = energy of first reduction couple, *vs.* nhe.
iv) $c^+/c^* = c^+/c - \mathrm{Exen}$
v) $c^*/c^- = \mathrm{Exen} + c/c^-$
vi) $Q_{ox} = -0.44 - c^+/c^*$
vii) $Th_{ox} = c^+/c - 0.82$
viii) $Q_{red} = c^*/c^- - 0.82$
ix) $Th_{red} = -c/c^- - 0.44$
x) $Bac_{ox} = 0.44 + c^+/c$
xi) $Bac_{red} = 0.82 - c/c^-$

Where $E^\circ(\mathrm{MV^{2+}/MV^+}) = -0.44$ V and $E^\circ(\mathrm{TEOA^+/TEOA}) = +0.82$ V. In some literature reported cases c^*/c^- and c^+/c^* are available from quenching experiments.

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