Long wavelength sensitizers for europium(III) luminescence based on acridone derivatives

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The preparation of several acridone derivatives which have been shown to act as sensitizers for europium(III) luminescence at wavelengths longer than 400 nm is described. The efficiency of sensitization increases as the chromophore is held closer to the ion and the inner sphere hydration number of the ion lowered.

Background

Sensitization of lanthanide ion luminescence, in particular that of the europium and terbium trivalent ions, has been exploited in the development of a number of useful signalling systems for time-resolved assays.[1,2] The energetics of sensitized emission from these ions dictates that these complexes must be excited with ultraviolet light, a case highlighted by Steemers *et al.*[3] who estimated that the absorption edge of the sensitizer cannot be much above 346 nm for Tb^{3+} and 385 nm for Eu^{3+} complexes. However, it would be preferred if excitation wavelengths could be moved further towards the visible region, first because shorter wavelengths are strongly absorbed by nucleic acids, aromatic amino acids and reduced pyridine nucleotides such as NADH, which can contribute to decreased assay sensitivities and, second, as shorter wavelengths require expensive quartz optics. Thus there is a need for systems that operate using significantly longer wavelengths for excitation. One approach has been to develop complexes of the near infrared emitting lanthanide ions such as ytterbium(III),[4] and neodymium (III)[5] although commercial instruments for routinely measuring these emissions, at wavelengths >800 nm, are not yet available. An alternative, described herein, is to optimise sensitization of europium ions by using sensitizers that are stimulated at wavelengths >400 nm (see Fig. 1).

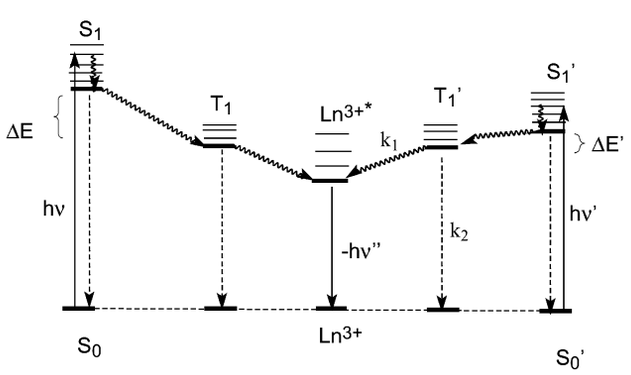
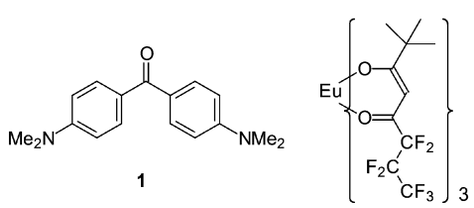


Fig. 1 Proposed scheme: smaller singlet to triplet energy gap ($\Delta E' < \Delta E$) allows irradiation of the sensitizer at lower energies (longer wavelengths). The efficiency of lanthanide emission depends on the efficiency of the triplet energy transfer (k_1) *versus* other decay processes, such as internal conversion (k_2). Simplified scheme; other processes, such as back energy transfer, not depicted.

During the course of our work, it was reported by Verhoeven and co-workers[6] that the excitation window for Eu^{3+} complexes can be extended to longer wavelengths by such appropriate selection of the sensitizer. Visible light, intermolecular sensitization of Eu^{3+} was therein reported for solutions of Michler's ketone **1** and $Eu(fod)_3$ (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dione) **2** in benzene. The excitation spectrum for this emission showed a maximum at 414 nm, the band extending beyond 450 nm and this new absorption band, which was not observed in the absence of **2**, was attributed to be the solvent-dependent $S_0 \longrightarrow S_1$ transition of the carbonyl moiety of **1** in the **1**·**2** complex. Other complexes, involving ketone-containing chromophores derived from acetophenone[7] and benzophenone,[8] have also been reported. The benzophenone-conjugated europium and terbium complexes of ligand **3** have been reported to show strong absorption bands under neutral conditions extending to 370 nm, with emission quantum yields of 0.095 and 0.27 respectively.



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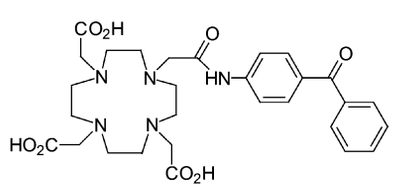

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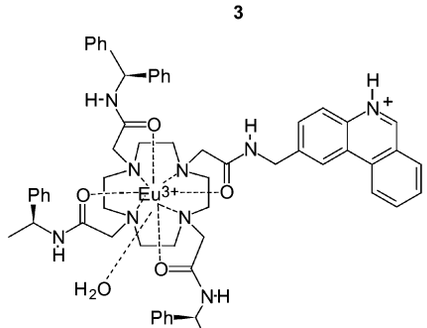

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Phenanthridine has also been incorporated as a sensitizer in the octadentate europium complex **4**. This is a pH sensitive

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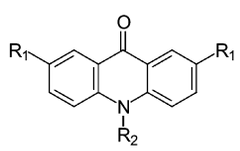
Table 1 Photophysical properties of Michler's ketone **1** and acridones **5** and **6**

Compound	Solvent	$E(S_1)/cm^{-1}$	Φ_{fl}	$E(T_1)/cm^{-1}$	Φ_{isc}	$\Delta(S - T)/cm^{-1}$
1[a]	Non-polar	—	—	—	0.91	—
1[a]	Polar	24670	—	21330	0.47	3340
5[a]	Non-polar	25430	0.015	20370	0.99	5060
5[b]	Polar	24425	0.75	21050	0.014	3375
6[b]	Polar	24510	0.56	20200	0.085	4310

[a] Ref. 33. [b] G. A. Val'kova *et al.*, ref 13.

probe and, on protonation, an excitation band at 370 nm forms.[9]

Our interest focused on the use of acridone **5**, which is widely used as a label and chemosensor in fluorescence-based assays.[10,11] Advantages of acridone include its chemical inertness and its photochemical resistance to bleaching. Its photophysical properties are listed in Table 1, from which it can be seen that, in polar solvents, fluorescence predominates over intersystem crossing to the triplet state. It has been shown, however, that intersystem crossing can be induced by proximity of lanthanide ions to fluorophores by the external heavy atom and paramagnetic effects.[4,12] The triplet energy level for free acridone in polar solvents is around 21050 cm^{-1},[13] which lies too close in energy to the emissive $^5D_4$ level of Tb^{3+} at 20400 cm^{-1} to observe efficient and irreversible terbium-centred luminescence, but which should be sufficient to excite the $^5D_1$ level of Eu^{3+} ions.

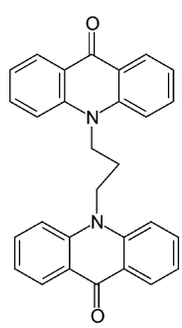


5, $R_1 = R_2 = H$

6, $R_1 = Br$, $R_2 = H$

7, $R_1 = H$, $R_2 = Et$

8, $R_1 = Br$, $R_2 = Et$



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We were also interested in 2,7-dibromoacridone derivatives **6**, since in these an *internal* heavy atom effect operates and it was of interest to ascertain whether or not this would assist in the intersystem energy sensitization of adjacent lanthanide ions. It is known that, for 2-bromoacridone, intersystem crossing between the singlet and triplet states is enhanced (see Table 1).[11]

Herein, we describe the results of the addition of simple *N*-alkylated-acridone **7** and its 2,7-dibromo-analogue **8** to $Eu(fod)_3$ to evaluate their ability to act as sensitizers for europium(III) luminescence. Thereafter we describe the synthesis of some polyaminocarboxylate ligands that incorporate the acridone group as a sensitizer and present a detailed photophysical study of the complexes of these ligands with europium(III).

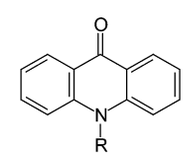
Results and discussion

Synthesis of the ligands

Acridone itself is a pale yellow solid with a sharp melting point above 350 °C and possessing very poor solubility in most organic solvents. This high melting point and insolubility reflects the highly associated nature of the solid: strong intermolecular NH···O hydrogen bonds and strong π–π stacking interactions exist between the planar molecules.[14] Because of these solubility difficulties, relatively few reports on its chemistry appear in the literature.[15] Formation of *N*-alkyl derivatives allows a means for attaching the nucleus to ligands whilst also rendering the group more soluble.

Initially the *N*-ethyl derivatives **7** and **8** were prepared using the method of Nishi *et al.*,[16] which employs aqueous butan-2-one as solvent and *N*-benzyltriethylammonium hydroxide as base. Vigorous stirring is required in order to aid the dissolution of the acridones as reaction proceeds. In contrast to the starting acridones, both the products were soluble in organic solvents, such as hot ethanol, from which the products were recrystallized, benzene and acetonitrile, allowing intermolecular studies to be performed with $Eu(fod)_3$.

For intramolecular studies efforts were made to incorporate the acridone units into some cyclen derivatives (cyclen = 1,4,7,10-tetraazacyclododecane), known to form kinetically stable ligands with the lanthanides. These required the corresponding *N*-bromoalkylacridone intermediates. Applying the earlier methodology to prepare the *N*-bromoalkylacridone **10** by use of 1,3-dibromopropane failed, the only product isolated being the di-substituted product **9** even when using an excess of the alkylating agent. It is thought that alkylation occurs on the surface of the insoluble acridone where the local concentration is high and di-alkylation occurs preferentially.



10, $R = (CH_2)_3Br$

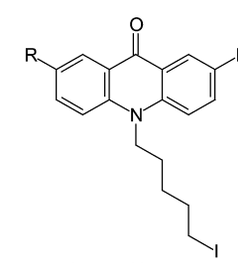
11, $R = CH_2CH{=}CH_2$

12, $R = (CH_2)_3Cl$

13, $R = (CH_2)_2Br$

14, $R = (CH_2)_2O$-(tetrahydropyranyl)

15, $R = CH{=}CH_2$



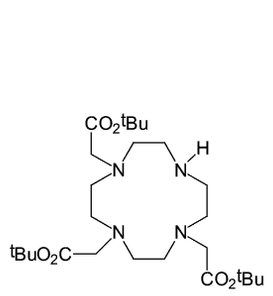
16, R = H

17, R = Br

The potassium salt of *N*-acridone was then prepared using potassium hydroxide in ethanol and the dry salt reacted with an excess of 1,3-dibromopropane. However the product was a mixture of the desired bromopropyl acridone **10** and a new compound, identified as the elimination product, *N*-allylacridone **11**. Formation of the latter was confirmed by direct preparation from acridone using allyl bromide as alkylating agent.[17]

Since the mixtures of **10** and **11** proved very difficult to separate, by either crystallization or column chromatography, one further alkylation was attempted, using 1-bromo-3-chloropropane, in the hope of selective alkylation at the bromide terminus. In the event, using *N*,*N*-dimethylformamide as solvent and sodium hydride as base, a mixture of three products was obtained: the bromide **10**, the alkene **11** and the chloride **12**, again as a mixture that was very difficult to separate.

In order to decrease the polarity of the system, we then turned to the pentyl homologue. Using 1,5-diiodopentane as alkylating agent and the sodium salt of the acridone (NaH



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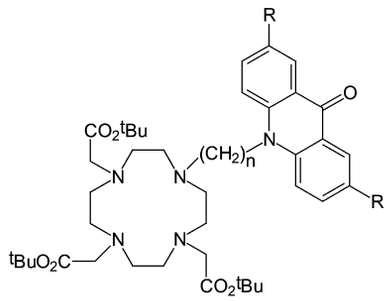
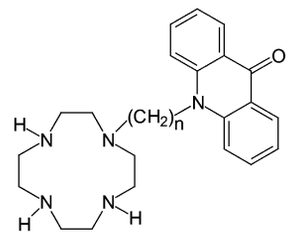


19, R = H, n = 5

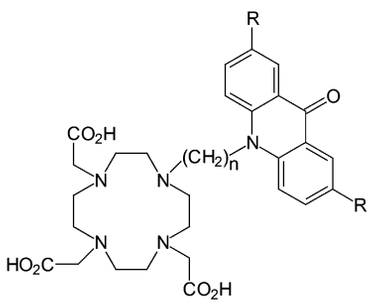
20, R = Br, n = 5

21, R = H, n = 2



22, n = 5

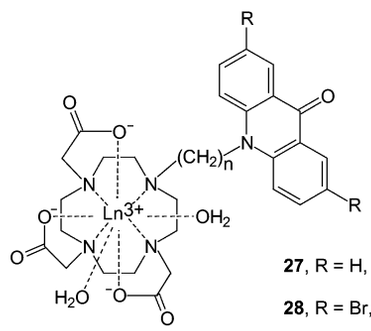
23, n = 2



24, R = H, n = 5

25, R = Br, n = 5

26, R = H, n = 2



27, R = H, n = 5, Ln = Eu

28, R = Br, n = 5, Ln = Eu

29, R = H, n = 2, Ln = Eu

30, R = H, n = 5, Ln = Gd

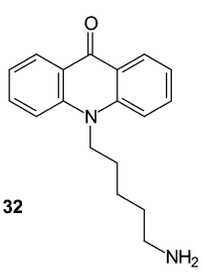
31, R = Br, n = 5, Ln = Gd

in DMF) selective mono-alkylation *was* achieved to form the required *N*-(5-iodopentyl)acridone derivative **16**; the dibromoacridone-derivative **17** was also prepared in this manner. Under these conditions elimination of the pendant iodoalkyl group to the corresponding alkene was not observed.

Preparation of the substituted cyclen **19** was initially attempted by alkylation of the tri-substituted cyclen **18** with the iodopentylacridone **16**. A direct synthesis of the tris-*tert*-butyl ester of DO3A (1,4,7,10-tetraazacyclododecan-1,4,7-triethanoic acid) **18** was reported by Parker *et al.*,[18] who showed that selective tri-alkylation of three of the four ring nitrogens in cyclen could be achieved, the fourth nitrogen being rather sluggish towards alkylation under mild conditions. This avoids the original route to DO3A derivatives, which requires prior protection of the fourth nitrogen.[19]

The reaction between compounds **16** and **18** proved to be extremely sluggish and only poor yields of the required product **19** could be obtained after refluxing the reactants in acetonitrile for several days, longer periods of heating causing general degradation. A similar result was obtained with the dibromide **17**, affording the triester **20**. As an alternative route to compound **19**, the selective mono-alkylation of cyclen was initially carried out to form compound **22** in good yield (89%), followed by tri-alkylation with *tert*-butyl bromoacetate. This procedure yielded the required ester **19** in 67% yield. Removal of the protecting groups, using trifluoroacetic acid, yielded the required tri-acid **24**. Deprotection of the dibromo-analogue **20** likewise afforded the tri-acid **25**. Samples of the acids **24** and **25** were then reacted with europium chloride, to form the neutral salts **27** and **28** respectively, and gadolinium chloride, to form the salts **30** and **31**.

A linear analogue of the chelate **27** was also prepared from DTPA (diethylenetriaminepentaacetic acid) for comparative purposes in the photophysical study. The iodopentylacridone derivative **16** could be reacted with ammonia, in dichloromethane in a sealed tube at 60 °C for several days, to afford the hydroiodide salt of the corresponding amine **32**. This amine could be reacted with DTPA anhydride **33** to give the monoamide, which was immediately loaded with europium(III) chloride and isolated as the sodium salt of complex **34**.



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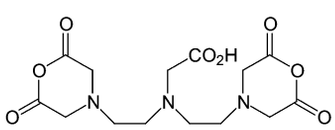

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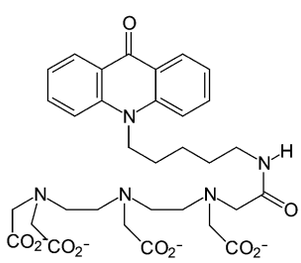
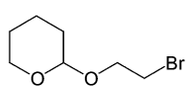


Eu^{3+},Na^{+}

34



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Some preliminary results with complexes **27** and **28** were recently reported.[20] Developing on the observations with the pentyl chains, one final cyclen derivative was also prepared, that with a shorter handle to the acridone chromophore. The target selected was the cyclen conjugate **26** which was synthesised from *N*-2-bromoethylacridone, which was finally obtained using a revised approach to the preparation of the shorter-chained haloalkylacridones. Since tetrahydropyranyl ethers can be converted directly into the corresponding bromides,[21]

acridone was alkylated with the tetrahydropyranyl ether of bromohydrin **35** to give the derivative **14** in good yield (79%). Treatment of the latter with triphenylphosphine and carbon tetrabromide smoothly gave the required bromoethyl derivative **10**. Attempted alkylation of the cyclen tri-ester **18** failed, elimination being observed to give the ethene **15** so the mono-alkylation of cyclen, to give compound **23**, was initially carried out, followed by trialkylation with *tert*-butyl bromoacetate to give compound **21**. Deprotection to tri-acid **26**, using trifluoroacetic acid, followed by loading with europium gave the required two-carbon linked probe **29**.

Intermolecular studies

Initially, intermolecular studies were carried out using the *N*-ethyl derivatives **7** and **8** since these were more soluble than the rather intractable parent compounds. These were compared to the interaction of Michler's ketone **1** with the europium(III) diketone **2**. In contrast to the solvent dependent absorption band from the **1**·**2** complex, the acridone derivatives **6** and **7** are inherently yellow and display absorption bands at around 415 nm regardless of solvent polarity.

Typical spectra obtained are illustrated in Fig. 2, key data

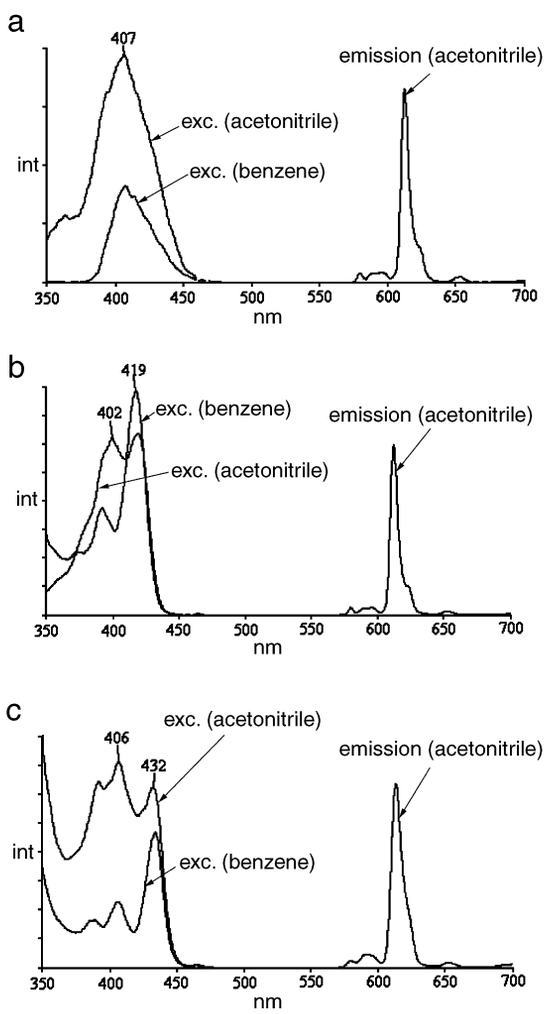

Fig. 2 Excitation and emission spectra illustrating the intermolecular sensitization of compound **2** upon excitation into the long wavelength bands of Michler's ketone **1** and acridone sensitizers **7** and **8**. 1 : 1 ratios of sensitizer to europium complex **2** at *ca.* 1×10^{-5} mol dm^{-3}. (a) With **2**; (b) with **7**; (c) with **8**.

being given in Table 2. Even in acetonitrile solution the acridones **7** and **8** act as sensitizers for complex **2**, most probably as a result of energy transfer from their excited triplet states. The characteristic emission curve of Eu^{3+} emission was observed in both cases. The luminescence could be observed by excitation of the peaks at 419 nm in the case of compounds **6** and **7** and at 439 nm for the dibromide **8**. These represent the longest wavelength excitation peaks ever recorded for europium complexes measured in a polar solvent.

Intramolecular studies

Aqueous solutions of the free ligand **24** showed absorption maxima at 257 (35000), 394 (5300) and 410 nm (5300 dm^3 mol^{-1} cm^{-1}) respectively. The absorption spectrum was not significantly changed upon forming europium (III) complex **27**, suggesting that the acridone moiety does not itself coordinate with the lanthanide centre. The dibromide derivative **25** showed absorption bands at 260 (27800), 285 (27300), 407 (5200) and 427 (5200), again relatively unperturbed upon formation of complex **28**. The luminescence excitation spectra of the two complexes mirrored their respective UV absorption profiles.

From the lifetime measurements of the complexes, carried out in water and deuterium oxide (Table 3), the calculated inner sphere hydration value, q' (see Experimental section),[9] showed that around an average of 2.2 molecules of water were coordinated around the europium(III) ions in each case, in accord with that observed in other, related, seven-coordinate DO3A-derived complexes.[22]

The analogous gadolinium complexes **30** and **31** (*cf.* **27** and **28**) were also prepared from the ligands **24** and **25** and used to measure the triplet energy levels of these complexes at 77 K in an aqueous glass (see Table 3).[23] As expected, the triplet level of the dibromoacridone complex **31**, at 19800 cm^{-1}, was lower in energy by some 1700 cm^{-1} compared to the parent acridone complex **30**, at 21500 cm^{-1}, although this was still high enough to act as a sensitizer for excitation of the $^5D_0$ emissive level of europium(III), at 17250 cm^{-1}, without observing significant back energy transfer.

A study on the effect of deoxygenation of the solutions of europium(III) complex **27** led to a slight increase in the intensity of emission, however there was *no* observed change in the lifetime of the luminescence. The increased emission intensity suggests that the acridone chromophore may be susceptible to quenching by molecular oxygen whilst, more importantly, the constancy of the lifetime of the luminescence of the europium ion in the presence and absence of oxygen strongly suggests that back energy transfer from the populated $^5D_0$ state of the ion to the acridone donor state is insignificant. These results support a triplet-mediated sensitization mechanism and this was further substantiated by observation of a short-lived band corresponding to the aryl triplet level from solutions of the complex **27**, in an aqueous glass at 77 K.

Quantum yield measurements required the use of a reference material, compound **4**, which at pH 1.5 shows a quantum emission yield of 0.021.[9] Measurements were carried out on a range of solutions at different absorbance values using the integrated emission signal (see Experimental section).

Emission output of the excited europium ion depends, amongst other factors, on the efficiency (rate) of the energy transfer process from the acridone sensitizer attached *via* the linker chain. In this system the sensitizer is not an intrinsic chelating group and a through space energy transfer process is involved. Some studies on variations of intramolecular, sensitized luminescence with linker length have been reported. Parker and co-workers showed, for some phenanthridinium chelates related to **4**,[9] that intramolecular energy transfer occurs by a Förster coupled dipole mechanism.[24]

It was of interest, therefore, to compare the results for the C_5-linked group, as in **27**, with the results from the C_2-linked complex **29**. The four-fold increased quantum yield (ϕ_{H_2O} 0.053 compared to 0.014) for the shorter linker requires this step to be more efficient; the lifetime studies show that there is no extra

Table 2 UV-vis absorption data[a]

Compound	Solvent	Without **2**		With **2**	
		λ_{max}/nm	ε/dm^3 mol^{-1} cm^{-1}	λ_{max}/nm	ε/dm^3 mol^{-1} cm^{-1}
1	Benzene	348	35000	414	30000
	Acetonitrile	353	32000	353	38700
7	Benzene	379	8800	379	6000
		398	12700	398	11600
		—	—	425	7500
	Acetonitrile	381	6000	381	7500
		400	8400	400	9800
8	Benzene	395	7600	395	7200
		418	10200	415	10700
		—	—	435	2500
	Acetonitrile	395	6200	395	6800
		415	7900	416	8500

[a] Typical concentrations of free and complexed ligands were 10^{-4} mol dm^{-3}.

Table 3 Photophysical data for complexes **27**, **28**, and **29**

Compound	λ_{exc}/nm[a]	τ_{H_2O}/ms	τ_{D_2O}/ms	q'	$\Delta E(T_1)$/cm^{-1}[b]	ϕ_{H_2O}[c]	ϕ_{D_2O}[c]
27	395, 406	0.37	1.67	2.2	21500	0.014	0.035
28	406, 428	0.38	1.52	2.1	19800	0.010	0.025
29	395, 406	0.35	1.20	2.1	—	0.053	0.126

[a] Longer wavelengths only. [b] Measured from the Gd^{3+} complexes at 77 K in an aqueous glass. [c] Measured in aerated solution (λ_{exc} 380 nm), using **4** as reference, see Experimental section.

shielding of the lanthanide ion when the acridone group is held nearer. The luminescence is enhanced in **29** because there is a reduced degree of conformational freedom of the chromophore about the shorter chain and the sensitizer is held in a fairly confined conformational space never more than *ca.* 4 Å from the ion. The conformational space allowed for the acridone group in compound **27** is greater with the flexible C_5-linker but, on average, is further away from the ion.

Further confirmation of the importance of holding the acridone sensitizer within range for the Förster energy transfer was obtained using the DTPA derived complex **34**. In this complex, the DTPA functional groups more fully saturate the ion, a q' value of about 1 molecule of water being obtained, as expected for the octadentate ligand. Despite this, the strength of the emission signal was much weaker than obtained for the cyclen complexes, **27** and **29** as a consequence of the even longer linker group resulting from the amide conjugation and the less efficient intramolecular energy transfer step.

The observed quantum yield results indicate that, for the bromoacridone cyclen complex **28**, the presence of the bromine substituents plays no major role in enhancing the efficiency of the initial singlet to triplet transition by the heavy atom effect. The slight decrease in quantum yield (from ϕ_{H_2O} 0.014 for **27**, to ϕ_{H_2O} 0.010 for **28**) can be explained by the narrowing of the triplet–excited Eu^{3+} energy gap. Presumably, the paramagnetic electromagnetic effects induced by the chelated europium ion are sufficient to induce the required singlet–triplet energy transfer process.

In the complexes **27**, **28** and **29**, the europium ion remains coordinatively unsaturated. It was of interest to study the effect of saturating these extra coordinating sites.[25] Rather than undertaking the synthesis of new ligands, the effect of the addition of various oxygen-donor ions that can compete with bound water was studied, using the shorter linked complex **29**. The anions used were citrate, tartrate and phosphate, all made up in buffers at pH 7.5 and their effects on the europium emission lifetimes at various ion concentrations were measured (Table 4). In all cases the intensity of the emission spectrum increased. Citrate proved to be most effective, leading to a 5-fold increase in the quantum yield of emission in the presence of an excess of citrate ($\phi_{citrate} \approx 0.26$) with an approximately 4-fold increase in the presence of either phosphate or tartrate donors ($\phi_{tartrate} \approx \phi_{phosphate} \approx 0.20$). Using phosphate buffered saline (PBS), which contains between 0.01 and 0.1 mol dm^{-3} phosphate, complex **29** gave a lifetime in the order of 0.5 ms and a q' value of 1, reflecting the replacement of an average of one molecule of water from the coordination sphere of the Eu^{3+} ion and a doubling of the quantum yield to $\phi_{PBS} \approx 0.10$.

Table 4 Effect of anion additions to **29**[a]

Salt concn./mol dm^{-3}	Lifetimes (τ/ms)		
	Citrate[b]	Phosphate[b]	Tartrate[b]
0	0.35	0.35	0.35
1×10^{-5}	0.35	0.35	0.35
1×10^{-4}	0.36	0.36	0.5
1×10^{-3}	0.43	0.37	0.79
1×10^{-2}	0.65	0.41	0.90
1×10^{-1}	0.88	0.61	0.94
1	0.91	0.74	—
q'[c]	~0.0	0.3	~0.0

[a] Complex at 1×10^{-5} mol dm^{-3}, see Experimental section for details. [b] Solutions made up from 1.0 mol dm^{-3} stock solutions of trisodium citrate, disodium hydrogen phosphate–potassium dihydrogen phosphate and 1×10^{-1} mol dm^{-3} potassium sodium tartrate respectively. [c] The q' values (see ref. 9) were those obtained at the maximum concentrations of added salts.

Thus, under typical assays conditions, this model complex should be an efficient luminescent label, in addition to the advantages of the complex being very stable, and water soluble, owing to the carboxylate macrocyclic backbone. The excitation, at wavelengths greater than 400 nm, should help to increase assay sensitivities by reducing the extent of simultaneous absorption of light by fluorescent biological molecules and thereby eliminating a source of error.

Experimental

The lanthanide luminescence spectra were measured on a Perkin-Elmer LS50B luminescence spectrometer, using FLWinLab software. Excited state lifetimes were acquired using

the *Lemming* software package developed by Dr A. Beeby, University of Durham. The results quoted represent the average of at least 20 scans and a minimum of 3 lifetime measurements for each sample being measured. The presence of a single light-emitting species, with no quenching by other excited state molecules, was confirmed by the observation of mono-exponential decays.

No improvement of fit (as judged by randomness of residual and reduced chi squared values) was observed upon fitting to a double exponential decay.

The number of coordinated water molecules around the lanthanide ions in their complexes were determined using Parker's equation,[26]

$$q' = A'_{Ln}[(k_{H_2O} - k_{D_2O}) + corr_{Ln}] \quad (1)$$

where q' is the inner sphere hydration number, k is the rate constant for depopulation of the lanthanide excited state in H_2O and D_2O respectively. For europium(III), $A'_{Eu} = 1.2$ ms and $corr_{Eu} = -0.25$ ms^{-1}; for terbium(III), $A'_{Tb} = 5$ ms and $corr_{Tb} = -0.06$ ms^{-1}.

Degassing of samples was carried out in a cell equipped with a 10 mm pathlength square cuvette and a degassing bulb; degassing was achieved using four 'freeze–pump–thaw' cycles and the samples were measured under vacuum. Low temperature phosphorescence spectra studies on the gadolinium(III) complexes, for determining chelate triplet energies, were obtained using an Oxford Instruments optical cryostat with the samples contained in 10 mm cuvettes. The triplet energy was obtained from the highest energy (shortest wavelength) phosphorescence band, corresponding to the 0–0 transition.

Quantum yield measurements were recorded relative to that of chelate **35** in water and acidified with a few drops of trifluoroacetic acid, using the reported value of $\phi = 0.021$ (H_2O, pH 1.5).[9] Solutions with different absorbances, between 0.05 and 0.11, were used to ensure the same amount of light was absorbed by both the standard and the sample at the common wavelength of 380 nm. For each sample/standard pair, the total integrated emission upon excitation at this wavelength was measured under identical instrument and ambient conditions. A plot of total integrated emission (E) against absorbance (A) then gave a straight line with slope E/A. The unknown quantum yield, ϕ_x can then be calculated from the equation,[27]

$$\phi_x = \phi_r(\text{slope}_x/\text{slope}_r)(n_x/n_r)^2 \quad (2)$$

where r and x refer to the reference and unknown respectively and n is the refractive index of the solution. Since $n_x \approx n_r$ the equation is simplified to the ratio of the two slopes. Generally stock solutions of the ligands and complexes were made up as specified, in distilled water, deuterium oxide (Aldrich, 99.9%) or 10^{-3} mol dm^{-3} HEPES solution [HEPES is *N*-(2-hydroxyethyl)piperazine-*N*′-ethanesulfonic acid] at pH 7.4. Samples to be measured were made up to volumes of 4 cm^3 in their working concentrations, then 2.5 cm^3 of the solution was transferred to a clean 10 mm quartz cuvette, using electronic Rainin pipettes. Luminescence measurements were carried out immediately and repeated after 12 h to ensure equilibration/stability. During the course of a series of measurements the cuvettes were rinsed thoroughly with distilled water, then methanol and air-dried. When not in use the cuvettes were soaked in a solution of Caro's acid.

Mps were determined on a Kofler hot stage apparatus and are uncorrected. Ultraviolet–visible spectra were determined on a Unicam PU8700 Series spectrophotometer using 10 mm cells; absorption maxima (λ_{max}) and corresponding molar absorption coefficients (ε_{max}) are reported in nm and dm^3 mol^{-1} cm^{-1} respectively. Infrared spectra were recorded on a Perkin Elmer System 2000 FTIR spectrophotometer as thin films for liquids or as either Nujol mulls or KBr discs on solids or as solutions in chloroform. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AC300 spectrometer at 300 and 75 MHz respctively, using TMS as internal reference. Chemical shift values (δ) are quoted in ppm while observed coupling constants are reported: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad; and ex, exchangeable with D_2O. Mass spectra were recorded by the EPSRC National Mass Spectrometry Service Centre, Swansea.

Solvents were dried and purified according to literature methods.[28] Thin layer chromatography was carried out on either Merck 0.25 mm pre-coated 60 F_{254} silica gel on glass plates or Merck 0.25 mm 60 F_{254} neutral alumina on glass plates. Column chromatography was carried out using either Fluka silica gel 60 (220–240 mesh) or Fisher Scientific Activated Neutral Aluminium Oxide (100–1250 mesh); grading of the alumina was according to the literature method.[8] Solvent ratios refer to volumes prior to mixing. Solutions were dried over anhydrous sodium sulfate. 1,4,7,10-Tetraazacyclododecane (cyclen) was obtained from Strem Chemicals, USA and acridone from Sigma Aldrich Co. Ltd, Poole, Dorset, UK. Sodium hydride was a 60% w/w suspension in mineral oil; weights of sodium hydride used are reported. Ether refers to diethyl ether.

Synthesis

2,7-Dibromoacridone 6. Prepared by the reported method[29] using acridone (2.0 g, 10 mmol) in acetic acid (250 cm^3) and bromine (4.1 g, 26 mmol). The obtained solid was recrystallized (2×) from hot *N*,*N*-dimethylformamide to afford the dibromide as yellow needles (1.77 g, 49%), mp > 300 °C (lit.[30] 438 °C).

***N*-Ethylacridone 7.** Prepared by the method of Nishi *et al.*[16] The product was crystallized from ethanol to give the title compound as yellow plates (46% yield), mp 158–159 °C (lit.[16] 158–160 °C); λ_{max} (benzene) 280 (12600), 379 (8000), 398 (11900); ν_{max} (Nujol) 1634, 1608, 1595, 1265, 1173 cm^{-1}; δ_H ($CDCl_3$) 1.57 (3H, t, *J* 7.5, CH_2CH_3), 4.48 (2H, q, *J* 7.5, NCH_2CH_3), 7.30 (2H, t, *J* 7.5, 2,7-H), 7.53 (2H, d, *J* 8, 4,5-H), 7.74 (2H, td, *J* 8 and 1, 3,6-H), 8.59 (2H, dd, *J* 8 and 1, 1,8-H); δ_C ($CDCl_3$) 12.7, 41.1, 114.5, 121.3, 122.7, 128.1, 134.0, 141.6, 178.4; *m*/*z* (CI) 224 (MH^+, 100%).

2,7-Dibromo-*N*-ethylacridone 8. 1-Bromoethane (0.09 g, 1.5 eq., 0.85 mmol) was added dropwise to a stirred slurry of 2,7-dibromoacridone **6** (0.20 g, 0.56 mmol) and benzyltriethylammonium chloride (10 mg) in butan-2-one (1 cm^3) and aqueous sodium hydroxide solution (1 cm^3, 10 mol dm^{-3}). The slurry was stirred at 60 °C for 3 h and then the mixture was poured into hot water (10 cm^3) and allowed to cool to room temperature. The solids were filtered off and recrystallised from ethanol to yield the *title product* (0.10 g, 44%), mp 225–226 °C (from EtOH) (Found: C, 47.3; H, 2.9; N, 3.6. $C_{15}H_{11}NOBr_2$ requires C, 47.3; H, 2.9; N, 3.7%); λ_{max} (benzene) 290 (35000), 395 (7000), 414 (10000); ν_{max} (Nujol) 1633, 1592, 1274, 1176 cm^{-1}; δ_H ($CDCl_3$) 1.54 (3H, t, *J* 7.5, CH_3), 4.40 (2H, q, *J* 7.5, NCH_2), 7.40 (2H, d, *J* 9, 4,5-H), 7.78 (2H, dd, *J* 2.5 and 9, 3,6-H), 8.63 (2 H, d, *J* 2.5, 1,8-H); δ_C ($CDCl_3$), 12.6, 41.5, 115.1, 116.7, 123.8, 130.5, 137.1, 140.2, 175.7; *m*/*z* (CI) 384, 382, 380 (MH^+), 304, 302 ($MH^+ - Br$), 224 ($MH^+ - 2Br$).

Attempted preparations of *N*-(3-bromopropyl)acridone 10. *Method A.* To a stirred slurry of acridone (0.58 g, 3 mmol) and benzyltriethylammonium chloride (30 mg) in butan-2-one (3 cm^3) and aqueous sodium hydroxide (3 cm^3, 10 mol dm^{-3}) was added, dropwise, 1,3-dibromopropane (0.90 g, 4.5 mmol). The mixture was stirred vigorously and heated to 65 °C for 3 h before pouring into hot water (20 cm^3). The slurry was allowed to cool to room temperature and the yellow precipitate was collected by filtration, washed with water, dried and recrystallized from dimethylformamide to yield *N,N-(propan-1,3-diyl)diacridone* **9** (0.45 g, 70%), mp >300 °C; ν_{max} (Nujol) 1634,

1596, 1494, 1290, 1178 cm^{-1}; δ_H [$(CD_3)_2SO$] 2.27 (2H, m, 2-CH_2), 4.82 (4H, m, 1,3-CH_2), 7.32 (4H, t, *J* 7.5, 2,2′,7,7′-H), 7.83 (4H, t, *J* 7.5, 4,4′,5,5′-H), 8.34 (4H, d, *J* 7.5, 1,1′,8,8′-H); δ_C [$(CD_3)_2SO$] 24.5, 42.0, 115.8, 121.4, 121.7, 126.9, 134.2, 141.4, 176.4; *m*/*z* (CI) 431 (MH^+, 25%), 236 (40), 222 (30), 208 (15), 196 (70); HRMS (ES^+), found: 431.1760 (MH^+); $C_{29}H_{23}N_2O_2$ requires 431.1759.

Method B. To a slurry of acridone (1.0 g, 5 mmol) in dry ethanol (15 cm^3) was added potassium hydroxide (0.30 g, 5 mmol) and the mixture heated to reflux for 15 min. The solvent was removed under reduced pressure, the solid potassium salt thus obtained mixed with 1,3-dibromopropane and the slurry was heated at reflux for 3 h. Petroleum ether was added to the cooled reaction mixture and the solids collected by filtration, washed with water and dried to yield a yellow solid (1.23 g). Examination of the product by ^1H NMR spectroscopy indicated a 1 : 1 mixture of mainly the desired bromide **10** and the elimination product **11**; δ_H ($CDCl_3$) for **10**: 2.51 (2H, m, 2-CH_2), 3.65 (2H, t, *J* 6.5, CH_2Br), 4.60 (2 H, t, *J* 8, NCH_2); for **11**: 4.98 (2H, m, NCH_2CH=CH_2), 5.10 (1H, dt, J_{trans} 17, 1.5, C*H*H=CH), 5.32 (1H, d, J_{cis} 10, C*H*H=CH), 6.16 (1H, m, CH_2C*H*=CH_2). Attempted separation by column chromatography failed.

Method C. To acridone (0.20 g, 1 mmol) in *N*,*N*-dimethylformamide (6 cm^3) was added sodium hydride (0.031g, 1.3 mmol) and the mixture was allowed to stir under nitrogen for 3 h at room temperature. 1-Bromo-3-chloropropane (0.56 cm^3, 7.5 mmol) was then added and the mixture heated at 80 °C with stirring for 4 h. The reaction was quenched by cooling and addition of water (10 cm^3) and the product was extracted with ethyl acetate (20 cm^3), which was then washed with water (3 × 10 cm^3). The organic phase was dried and evaporated to give a pale green solid. The crude product was chromatographed through silica gel, using 1 : 3 ethyl acetate–dichloromethane as eluent. One main fraction was eluted (0.045 g), shown to be a mixture of compounds **10**, **11** and **12** in an approximate ratio 45 : 45 : 10 respectively. This material was not further investigated.

***N*-(Prop-2-enyl)acridone 11.** Acridone (1.95 g, 10 mmol) was suspended in butan-2-one (10 cm^3) and aqueous sodium hydroxide (10 cm^3, 10 mol dm^{-3}) with benzyltriethylammonium chloride (60 mg) and the mixture stirred vigorously whilst adding allyl bromide (1.8 g, 15 mmol) slowly, dropwise. The mixture was warmed to 50 °C for 2.5 h and poured into hot water (25 cm^3) and cooled. The precipitated solids were collected by filtration and recrystallized from ethanol to afford the title compound as yellow crystals (1.75 g, 74%), mp 135–137 °C (EtOH) (lit.[17] 136–137 °C); ν_{max} (KBr) 1637, 1604, 1490, 1460, 1268, 1176, 937, 922 cm^{-1}; δ_H ($CDCl_3$) 4.96 (2H, m, NCH_2), 5.10 (1H, dt, J_{trans} 17 and 1.5, C*H*H=CH), 5.31 (1H, d, J_{cis} 10.5, C*H*H=CH), 6.14 (1H, m, C*H*=CH_2), 7.31 (2H, dd, *J*1.5 and 7.5, 2,7-*H*), 7.40 (2H, d, *J* 8.5, 4,5-*H*), 7.68 (2H, dt, *J* 1.5 and 7.5, 3,6-*H*), 8.55 (2H, dd, *J* 1.5 and 7.5, 1,8-*H*); δ_C ($CDCl_3$) 498, 115.4, 117.8, 121.8, 122.8, 128.0, 130.8, 134.2, 142.5, 178.5; HRMS (ES^+), found: 236.1077 (MH^+); $C_{16}H_{14}NO$ requires 236.1075.

***N*-(5-Iodopentyl)acridone 16.** To a slurry of acridone (0.39 g, 2 mmol) in anhydrous *N*,*N*-dimethylformamide (8 cm^3) was added sodium hydride (0.054 g, 2.25 mmol) and the mixture was stirred at room temperature under nitrogen for 6 h before adding 1,5-diiodopentane (2.60 g, 8 mmol) and heating the mixture with vigorous stirring to 60 °C for 16 h. The mixture was poured onto ice–water (20 g) and extracted with diethyl ether (30 cm^3) The organic phase was washed with brine (20 cm^3) and water (20 cm^3), dried, filtered and evaporated to afford a dark green solid. The material was chromatographed through silica gel, using 4 : 96 acetone–dichloromethane as eluant and the major fraction recrystallized from ethyl acetate to give the *title compound* as yellow crystals (0.49 g, 63%), mp 93–94 °C (Found: C, 55.5; H, 4.6; N, 3.5. $C_{18}H_{18}NOI$ requires C, 55.3; H, 4.6; N, 3.6%); λ_{max} (EtOH) 217 (20800), 253 (28000), 385 (9000), 403 (10700); ν_{max} (Nujol), 1636, 1591, 1275, 1173 cm^{-1}; δ_H ($CDCl_3$) 1.69 (2H, m, 3-CH_2), 1.94 (4H, m, 2,4-CH_2), 3.26 (2H, t, *J* 7, CH_2I), 4.37 (2H, t, *J* 8, NCH_2), 7.30 (2H, d, *J* 7.5, 2,7-H), 7.48 (2H, d, *J* 7.5, 4,5-H), 7.74 (2H, dt, *J* 2 and 7.5, 3,6-H), 8.59 (2H, dd, *J* 2 and 7.5, 1,8-H); δ_C ($CDCl_3$) 6.4, 26.2, 27.8, 32.9, 45.9, 114.5, 121.3, 122.5, 128.1, 134.0, 141.7, 178.0; *m*/*z* (CI) 392 (MH^+, 20%), 266 (MH^+ − I, 100).

2,7-Dibromo-*N*-(5-iodopentyl)acridone 17. To a slurry of 2,7-dibromoacridone **6** (0.71 g, 2 mmol) in anhydrous *N*,*N*-dimethylformamide (10 cm^3) stirred under nitrogen, was added sodium hydride (0.054g, 2.25 mmol) and the mixture stirred for 8 h to give a yellow solution. To the solution was added 1,5-diiodopentane and the solution was heated for 16 h at 60 °C before cooling and pouring onto ice–water (20 g) and extraction with ethyl acetate (50 cm^3). The extract was washed with brine (20 cm^3), water (20 cm^3), dried and evaporated under reduced pressure to afford a solid. Recrystallization from ethyl acetate afforded the *title compound* as yellow needles (0.45 g, 41%), mp 180–182°; λ_{max} (EtOH) 221, 254, 286, 398, 420 nm; ν_{max} (Nujol) 1635, 1597, 1274, 1174 cm^{-1}; δ_H ($CDCl_3$) 1.68 (2H, m, 3-CH_2), 1.93 (4H, m, 2,4-CH_2), 2.35 (2H, t, *J* 6.5, CH_2I), 4.30 (2H, t, *J* 8, NCH_2), 7.34 (2H, d, *J* 8.5, 4,5-H), 7.78 (2H, dd, *J* 2 and 9, 3,6-H), 8.61 (2H, d, *J* 2, 1,8-H); δ_C ($CDCl_3$) 6.3, 26.2, 27.8, 32.7, 46.4, 115.6, 116.7, 123.7, 130.5, 137.1, 140.3, 176.1; *m*/*z* (EI) 550, 548, 546 (M^+, 1 : 2 : 1, 50%), 423, 421, 419 (M^+ − I, 1 : 2 : 1, 25); HRMS (ES^+), found 547.8726 (MH^+); $C_{18}H_{17}NOBr_2I$ requires 547.8721.

***N*-[2-(2,3,4,5-Tetrahydropyran-2-yloxy)ethyl]acridone 14.** 2-(2-Bromoethoxy)tetrahydropyran **35** was prepared according to the literature method.[31] Acridone (0.49 g, 2.5 mmol) was suspended in anhydrous *N*,*N*-dimethylformamide (10 cm^3) with stirring and sodium hydride (0.067 mg, 2.8 mmol) added. The suspension was stirred for 6 h before adding the bromide (1.05 g, 5 mmol) and heating the mixture to 60 °C for 16 h. The cooled solution obtained was poured into water (10 cm^3) before extraction with ether (75 cm^3). The organic layer was washed with water (50 cm^3), brine (25 cm^3) and water (25 cm^3) before drying, filtering and evaporating to dryness under reduced pressure. The residual gum was triturated with petroleum ether to give the crude product as a yellow powder, before recrystallization from ethanol to give the title product (0.64 g, 79%) as yellow needles, mp 107–109 °C (Found: C, 74.1; H, 6.6; N, 4.3. $C_{20}H_{21}NO_3$ requires C, 74.3; H, 6.5; N, 4.3%); ν_{max} ($CHCl_3$) 3415, 1633, 1599, 1495, 1034 cm^{-1}; δ_H ($CDCl_3$) 1.53–1.68 (6H, m), 3.47 (1H, m, CHHO), 3.73 (1H, m, CHHO), 3.97 (1H, m, CHHO), 4.22 (1H, m, CHHO), 4.65 (3H, m, NCH_2 and C*H*O), 7.31 (2H, t, *J* 7.5, 2,7-H), 7.66 (2H, d, *J* 7.5, 4,5-H), 7.74 (2H, dt, *J* 1.5 and 7.5, 3,6-H), 8.58 (2H, dd, *J* 1.5 and 7.5, 1,8-H); δ_C ($CDCl_3$) 19.4, 25.4, 30.6, 46.1, 62.5, 64.5, 99.6, 115.2, 121.6, 122.6, 127.6, 128.0, 134.0, 142.4, 178.2; *m*/*z* (CI) 324 (MH^+, 100%).

***N*-(2-Bromoethyl)acridone 13.** The ether derivative **14** (0.65 g, 2 mmol) was stirred with carbon tetrabromide (1.33 g, 4 mmol) in freshly distilled acetonitrile (30 cm^3) at room temperature under argon before a solution of triphenylphosphine (1.05 g, 4 mmol) in dry acetonitrile (15 cm^3) was added, dropwise over 30 min. After a further 1 h, acetone (0.22 cm^3, 4 mmol) was added and the solution was stirred at room temperature for a further 16 h under argon. The solvent was removed under reduced pressure and the green residue treated with ethyl acetate (30 cm^3), the mixture filtered and the solution evaporated to dryness to give the crude product. The product was chromatographed through silica gel using dichloromethane–ethyl acetate mixtures (0–25% ethyl acetate).

The product was isolated as the major fraction and was crystallised from ethanol to give the *title product* as small yellow crystals (0.52 g, 85%), mp 169–170 °C (Found: C, 59.2, H, 4.0; N, 4.5. $C_{15}H_{12}NOBr$ requires C, 59.6: H, 4.0; N, 4.6%); λ_{max} (EtOH) 217 (14700), 254 (25600), 380 (4900), 397 (5700); ν_{max} ($CHCl_3$) 1633, 1601, 1493, 1263, 1178 cm^{-1}; δ_H ($CDCl_3$), 3.71 (2H, t, *J* 8.5, C*H*$_2$Br), 4.75 (2H, t, *J* 8.5, NC*H*$_2$), 7.35 (2H, t, *J* 7.5, 2,7-H), 7.49 (2H, d, *J* 8.5, 4,5-H), 7.78 (2H, dt, *J* 1.5 and 8, 3,6-H), 8.59 (2H, dd, *J* 1.5 and 8, 1,8-H); δ_C ($CDCl_3$), 25.7, 47.4, 114.1, 122.1, 122.7, 128.4, 134.5, 141.5, 178.0; *m*/*z* (CI) 304, 302 (MH^+, 100%).

1,4,7-Tris(*tert*-butoxycarbonylmethyl)-1,4,7,10-tetraazacyclododecane, hydrobromide salt 18·HBr. 1,4,7,10-Tetraazacyclododecane (1.78 g, 10 mmol) and sodium hydrogen carbonate (2.78 g, 33 mmol) were stirred in freshly distilled acetonitrile (60 cm^3) cooled to 0 °C under argon, whilst *tert*-butyl bromoacetate (6.45 g, 33 mmol) was added dropwise over 30 min. After the addition the reaction mixture was allowed to reach ambient temperature and stirred under argon for a further 48 h. The inorganic solids were removed by filtration and the filtrate evaporated under reduced pressure to leave a beige solid. Recrystallization from toluene afforded the title ester as a white solid (2.52 g, 42%), mp 178–180 °C (Found: C, 52.65; H, 8.6; N, 9.3. $C_{26}H_{50}N_4O_6$·HBr requires C, 52.4; H, 8.6; N, 9.4%); ν_{max} (Nujol) 3427, 2867, 2736, 1730, 1455, 1369, 1256, 1150 and 755 cm^{-1}; δ_H ($CDCl_3$), 1.47 (27H, s, *tert*-Bu), 2.89 (4H, s, 8,12-C*H*$_2$), 2.93 (8H, s, 2,3,5,6-C*H*$_2$), 3.10 (4H, s, 9,11-C*H*$_2$NH), 3.30 (2H, s, 4-C*H*$_2$CO$_2$), 3.38 (4H, s, 1,7-C*H*$_2$CO$_2$), 10.03 (2H, br s, ex, N*H*·*H*Br); δ_C (75 MHz, $CDCl_3$), 28.5, 47.8, 51.7, 58.5, 82.0, 170.0, 170.8; *m*/*z* (CI) 515(MH^+, 100%).

***N*-{5-[4,7,10-Tris(*tert*-butoxycarbonylmethyl)-1,4,7,10-tetraazacyclododecan-1-yl]pentyl}acridone 19.** To the triester hydrobromide **18·HBr** (0.30 g, 0.5 mmol) in acetonitrile (10 cm^3) stirred under argon, was added triethylamine (0.10 g, 1 mmol) and *N*-(5-iodopentyl)acridone **16** (0.195 g, 0.5 mmol). The mixture was heated to a gentle reflux for 30 h. The reaction mixture was then cooled, filtered and the filtrate evaporated to dryness under reduced pressure to leave a yellow gum. The product was dissolved in a minimum volume of chloroform and then chromatographed through neutral alumina, using 20 : 1 : 1 chloroform : methanol : isopropylamine as eluant, to yield, as one of the major fractions the *title compound* as an amorphous foam (85 mg, 22%); ν_{max} ($CHCl_3$) 2981, 2935, 2836, 1721, 1632, 1600, 1494, 1232, 1160 cm^{-1}; δ_H ($CDCl_3$) 1.31–1.45 (27H, br s, *tert*-Bu), 1.59 (4H, m, chain C*H*$_2$), 1.94 (2H, m, chain C*H*$_2$), 2.17–2.89 (18H, br m, ring and chain C*H*$_2$), 3.05 (2H, t, *J* 7.5, 2,7-H), 3.13 (4H, s, 4,10-C*H*$_2$CO$_2$), 4.38 (2H, t, *J* 8, ArNC*H*$_2$), 7.30 (2H, t, *J* 7.5, 1,8-H), 7.51 (2H, d, *J* 7.5, 4,5-*H*), 7.73 (2H, dt, *J* 1.5 and 7.5, 3,6-*H*), 8.58 (2H, dd, *J*, 1.5 and 7.5, 4,5-*H*); δ_C ($CDCl_3$) 23.3, 24.3, 27.1, 28.2, 46.0, 47.9, 50.5, 53.0, 53.4, 56.0, 57.1, 83.0, 115.2, 121.5, 122.5, 128.0, 134.3, 141.9, 170.2, 170.6, 178.7; *m*/*z* (FAB) 801 (M + Na^+, 80%), 779 (MH^+, 25).

2,7-Dibromo-*N*-{5-[4,7,10-tris(*tert*-butoxycarbonylmethyl)-1,4,7,10-tetraazacyclododecan-1-yl]pentyl}acridone 20. This compound was prepared in a manner similar to the unsubstituted acridone analogue **19**. Thus the *N*-iodopentyldibromoacridone **17** (0.165 g, 0.3 mmol) and the triester hydrobromide **18·HBr** (0.18 g, 0.3 mmol) and triethylamine (0.07g, 0.6 mmol) were heated together in acetonitrile (10 cm^3) at reflux for 48 h. Work-up and chromatography through neutral alumina afforded the *title product* (0.17 g, 60%) as a bright yellow gum. δ_H ($CDCl_3$) 1.432–1.52 (27H, m, *tert*-Bu), 1.74 (4H, m, chain C*H*$_2$), 1.87 (2H, m, chain C*H*$_2$), 2.18–2.95 (18H, br m, ring and chain C*H*$_2$), 3.04 (2H, s, 7-C*H*$_2$CO$_2$), 3.15 (4H, s, 4,10-C*H*$_2$CO$_2$), 4.38 (2H, t, *J* 7.5, ArNC*H*$_2$), 7.53 (2H, d, *J* 9, 4,5-H), 7.81 (2H, dd, *J* 2.5 and 9, 2,5-H), 8.59 (2H, m, 1,8-H); *m*/*z* (FAB) 960, 958, 956 (M + Na^+, 10 : 20 : 10%), 938, 936, 934 (MH^+, 8 : 15 : 8).

***N*-{5-[4,7,10-Tris(carboxymethyl)-1,4,7,10-tetraazacyclododecan-1-yl]pentyl}acridone 24.** The tri-ester **19** (0.40 g, 0.5 mmol) was taken in dichloromethane (5 cm^3) and to the solution was carefully added trifluoroacetic acid (5 cm^3). The solution was left stirring at room temperature for 24 h and the solvents then removed under reduced pressure. Dichloromethane (10 cm^3) was then added and evaporated off, twice, followed by two similar treatments with ether. The solid residue was taken up in a minimum of methanol and ether added dropwise, until the solution just turned cloudy, before leaving to stand overnight over an ether atmosphere. The crystalline powder was collected, washed with ether (2 × 5 cm^3) and dried to afford the *title acid* as a pale yellow powder (0.21 g, 67%), mp 144–146 °C; λ_{max} (H_2O) 217 (24800), 258 (39300), 395 (10000), 414 (10700); ν_{max} (Nujol) 3407 (br), 1724, 1689, 1596, 1290, 1267, 1180 cm^{-1}; δ_H ($CDCl_3$) 1.62 (2H, m, CH_2), 1.93 (2H, m, CH_2), 2.99–3.60 (24H, br, aza-ring C*H*$_2$), 4.58 (2H, t, *J* 8, ArNC*H*$_2$), 7.35 (2H, t, *J* 7, 2,7-H), 7.82 (4H, m, 3,4,5,6-H), 8.46 (2H, d, *J* 7.5, 1,8-H); δ_C (CD_3OD) 25.4, 25.6, 28.8, 47.4, 50.7, 50.8, 52.1, 53.9, 54.2, 56.5, 56.7, 117.6, 124.0, 129.2, 136.7, 144.1, 169.5, 175.7; *m*/*z* (FAB) 654 (M − H^+ + 2Na^+, 25%), 632 (M + Na^+, 100), 610 (MH^+, 25); HRMS (FAB), found: 610.3228 (MH^+); $C_{32}H_{44}N_5O_7$ requires 610.3241.

2,7-Dibromo-*N*-{5-[4,7,10-tris(carboxymethyl)-1,4,7,10-tetraazacyclododecan-1-yl]pentyl}acridone 25. The tri-ester **20** (0.15 g, 0.16 mmol) was stirred in 1 : 1 dichloromethane–trifluoroacetic acid (10 cm^3) for 24 h at room temperature. The solvent was removed under reduced pressure and acid chased off by the addition and evaporation of successive portions of dichloromethane (2 × 10 cm^3), methanol (2 × 10 cm^3) and then ether (2 × 10 cm^3). The obtained residue was dissolved in the minimum volume of methanol (0.25 cm^3), filtered and ether added dropwise until the solution just turned cloudy before storing under an atmosphere of ether overnight. The crystalline product was collected, washed with ether (2 × 5 cm^3) and dried to afford the *title acid* as bright yellow crystals (95 mg, 95%), mp 148–150 °C; λ_{max} (H_2O) 218 (28300), 260 (28900), 285 (28800), 406 (5900), 428 nm (5700); ν_{max} (Nujol) 3384 (br), 1682, 1621, 1590, 1279, 1205, 1133 cm^{-1}; δ_H (CD_3OD) 1.62 (2H, m, chain C*H*$_2$), 1.94 (4H, m chain C*H*$_2$), 3.06–3.69 (24H, m, chain C*H*$_2$, C*H*$_2$CO$_2$, aza ring C*H*$_2$), 4.43 (2H, t, *J* 7.5, ArN-C*H*$_2$), 7.63 (2H, d, *J* 9, 4,5-H), 7.83 (2H, dd, *J* 9 and 2, 3,6-H), 8.30 (2H, d, *J* 2, 1,8-H); δ_C (CD_3OD), 16.0, 25.3, 25.5, 48.0, 52.0, 53.8, 54.4, 56.6, 56.7, 117.0, 120.2, 124.9, 131.1, 139.3, 142.6, 169.7, 175.6, 177.7; *m*/*z* (FAB) 792, 790, 788 (M + Na^+); HRMS (ES^+), found: 788.1260 (M + Na^+); $C_{32}H_{41}N_5O_7{}^{79}Br_2Na$ requires 788.1270.

***N*-[5-(1,4,7,10-Tetraazacyclododecan-1-yl)pentyl]acridone 22.** To a solution of iodopentylacridone **16** (0.39 g, 1 mmol) in chloroform (10 cm^3) was added dropwise to a stirred slurry of cyclen (0.35g, 2 mmol) in chloroform (10 cm^3) under nitrogen over 30 min. The mixture was stirred for a further 16 h at room temperature before removing the solvent under reduced pressure. The residue was taken up in dichloromethane (15 cm^3) and acidified with hydrochloric acid (4 mol dm^{-3}). The aqueous layer was separated, then basified to pH 14 with concentrated sodium hydroxide solution and re-extracted with dichloromethane (4 × 10 cm^3). The organic extracts were combined, dried and evaporated to yield the title compound as a waxy yellow solid (0.40 g, 89%), mp 135–137 °C; ν_{max} (Nujol) 3292, 1634, 1599, 1489, 1259, 1185 cm^{-1}; δ_H ($CDCl_3$) 1.61 (4H, m, chain 3,4-C*H*$_2$), 1.92 (2H, m, chain 2-C*H*$_2$), 2.45–2.80 (18H, aza-ring C*H*$_2$, chain NC*H*$_2$), 4.31 (2H, t, *J* 8, ArNC*H*$_2$), 7.29 (2H, t, *J* 7.5, 2,7-H), 7.49 (2H, d, *J* 7.5, 4,5-*H*), 7.71 (2H, dt, *J* 1.5 and 7.5, 3,6-H), 8.55 (2H, dd, *J* 7.5 and 1.5, 1,8-H); δ_C

($CDCl_3$) 24.9, 27.3, 27.4, 45.3, 46.2, 46.4, 47.2, 51.7, 54.5, 114.8, 121.3, 122.4, 127.9, 134.0, 147.8, 178.0; *m/z* (CI) 436 (MH^+, 15%), 196 (acridone·H^+, 35).

Alkylation of the acridone–cyclen conjugate 22 to produce 19. To a solution of the cyclen derivative **20** (0.37 g, 0.8 mmol), in warm acetonitrile (25 cm^3) and triethylamine (0.47 g, 4 mmol) was added *tert*-butyl bromoacetate (0.95 g, 4 mmol) and the solution was then heated to reflux for 24 h. The reaction mixture was cooled and the solvent removed under reduced pressure. The residue was dissolved in dichloromethane (25 cm^3) and washed with aqueous sodium hydrogen carbonate solution (2 × 20 cm^3), followed by brine (20 cm^3). The organic layer was separated, dried, filtered and evaporated under reduced pressure to yield the tri-ester pentylacridone derivative **19** (0.50 g, 76%). The product ran as a single compound against the reference material described above and showed identical infrared and ^{1}H NMR spectra.. This material was used without further purification.

Attempted synthesis of *N*-{2-[4,7,10-tris(*tert*-butoxycarbonylmethyl)-1,4,7,10-tetraazacyclododecan-1-yl]ethyl}acridone 21. To a solution of the hydrobromide salt of the cyclen ester **18·HBr** (0.457 g, 0.79 mmol) in acetonitrile (10 cm^3) was added potassium carbonate (0.23 g, 1.66 mmol) and the mixture heated gently with stirring under argon for 30 min. To the mixture was then added, dropwise, *N*-(2-bromoethyl)acridone **13** (0.25 g, 0.83 mmol) in acetonitrile (5 cm^3). The mixture was then heated to a gentle reflux, with stirring, for a further 36 h before removing the solvent under reduced pressure and then partitioning the product between dichloromethane and water. The organic phase was washed with saturated aqueous sodium hydrogen carbonate (2 × 10 cm^3), then water (10 cm^3), dried, filtered and evaporated to dryness to leave a yellow solid. Recrystallization from ethanol gave a compound identified as *N-ethenylacridone* **15** (0.17 g, 92%) as yellow needles, mp 180–182 °C [lit.[32] 181.5 °C (EtOH)]; ν_{max} (Nujol) 1626, 1599, 1361, 1260, 1170, 996, 938 cm^{-1}; δ_H ($CDCl_3$) 5.69 (1H, d, J_{trans} 15.0, NCH=C*H*H), 6.03 (1H, d, J_{cis} 7.5, NCH=C*H*H), 6.71 (1H, dd, *J* 7.5 and 15.0, NC*H*=CH_2), 7.28 (2H, dt, *J* 1.5 and 7.5, 2,7-H), 7.62 (4H, m, 3,4,5,6-H); *m/z* (CI) 222 (MH^+, 100%).

***N*-[2-(1,4,7,10-Tetraazacyclododecan-1-yl)ethyl]acridone 23.** A solution of *N*-(2-bromoethyl)acridone **13** (0.40 g, 1.3 mmol) in dry chloroform (10 cm^3) was added dropwise to a solution of cyclen (0.45 g, 2.6 mmol) in dry chloroform (10 cm^3) stirred under nitrogen over 1 h. The solution was stirred for a further 24 h before evaporating under reduced pressure, partitioning between dichloromethane (15 cm^3) and hydrochloric acid (4 mol dm^{-3}, 5 cm^3). The acidic layer was separated and basified to pH 14 with concentrated aqueous sodium hydroxide solution and the mixture re-extracted with dichloromethane (2 × 15 cm^3). The organic extracts were combined, washed with brine (10 cm^3), dried and evaporated to dryness under reduced pressure to give the title compound as a waxy solid (0.36g, 69%); ν_{max} ($CHCl_3$) 3373, 1633, 1599, 1494, 1463, 1291, 909 cm^{-1}; δ_H ($CDCl_3$) 2.64–2.84 (16H, m, ring CH_2), 2.95 (2H, t, *J* 8, NCH_2), 4.54 (2H, t, *J* 8, ArNCH_2), 7.30 (2H, t, *J* 7.5, 2,7-H), 7.55 (2H, d, *J* 7.5, 4,5-H), 7.74 (2H, dt, *J* 1.5 and 7.5, 3,6-H), 8.58 (2H, dd, *J* 1.5 and 7.5, 1,8-H); δ_C ($CDCl_3$) 44.7, 45.4, 45.9, 47.0, 51.3, 52.8, 114.6, 121.6, 122.7, 128.2, 134.4, 141.9, 178.1; *m/z* (FAB) 406 (M + Na^+, 45%), 394 (MH^+, 100).

***N*-{2-[4,7,10-Tris(*tert*-butoxycarbonylmethyl)-1,4,7,10-tetraazacyclododecan-1-yl]ethyl}acridone 21.** To a solution of the ethylacridone derivative **23** (0.35 g, 0.88 mmol) and triethylamine (0.40 g, 4 mmol) in acetonitrile (25 cm^3) under argon was added *tert*-butyl bromoacetate (0.59 g, 3 mmol) and the solution was heated to a gentle reflux for 24 h. The solvent was removed under reduced pressure and the residue dissolved in dichloromethane (20 cm^3) and washed with water (3 × 10 cm^3) before drying, filtering and removal of the solvent under reduced pressure to afford the title ester as a light orange foam (0.55 g, 84%). This showed ν_{max} ($CHCl_3$) 2900, 1728, 1678, 1600, 1371, 1155 $cm.^{-1}$; δ_H ($CDCl_3$) 1.40–1.49 (27H, m, *tert*-Bu), 3.12–3.66 (24 H, br, aza-ring CH_2, CH_2CO_2, aza-NCH_2), 4.84 (2 H, m, ArNCH_2), 7.30 (2H, t, *J* 7.5, 2,7-H), 7.68 (2H, d, *J* 7.5, 4,5-H), 7.78 (2 H, t, *J* 7.5, 3,6-H) and 8.54 (2 H, d, *J* 7.5, 1,8-H); δ_C ($CDCl_3$) 28.1, 41.3, 50.9, 51.3, 51.9, 55.1, 55.8, 55.9, 56.0, 56.2, 114.4, 121.7, 122.8, 128.3, 134.5, 141.7, 169.4, 173.1, 178.0; *m/z* (CI) 737 (MH^+, 100%), 622 (25).

***N*-{2-[4,7,10-Tris(carboxymethyl)-1,4,7,10-tetraazacyclododecan-1-yl]ethyl}acridone 26.** The tri-ester **21** (0.50 g, 0.68 mmol) was stirred in dichloromethane (5 cm^3) and trifluoroacetic acid (5 cm^3) at room temperature for 3 h before adding a further portion of trifluoroacetic acid (2 cm^3) and stirring then continued for a further 16 h. The solvent was removed under reduced pressure, scourging twice with dichloromethane (2 × 5 cm^3) followed by methanol (2 × 5 cm^3) before adding methanol (5 cm^3) and then ether (15 cm^3) to afford a yellow precipitate. The solid was collected by filtration and then recrystallized from hot methanol to afford the *title compound* as a yellow powder (0.16 g, 40%), mp 178–180 °C; λ_{max} (H_2O) 216 (19000), 257 (43600), 395 (6500), 409 (6500); ν_{max} (Nujol) 3700 (br), 2800 (br), 1709, 1684, 1613, 1326, 1217, 1151 cm^{-1}; δ_H (D_2O) 3.17 (18H, br, CH_2N), 3.74 (2H, br, 7-CH_2CO_2), 3.80 (4H, br, 4,10-CH_2CO_2), 4.37 (2H, br s, ArNCH_2), 7.13 (2H, t, *J* 7.5, 2,7-H), 7.40 (2H, d, *J* 7.5, 4,5-H), 7.64 (2 H, t, *J* 7.5, 3,6-H), 7.93 (2H, d, *J* 7.5, 1,8-H); *m/z* (FAB) 590 (M + Na^+, 100%), 568 (MH^+, 35); HRMS (ES^+), found: 568.2774 (MH^+); $C_{29}H_{38}N_5O_7$ requires 568.2771.

***N*-(5-Aminopentyl)acridone 32.** *N*-(5-iodopentyl)acridone **16** (0.39 g, 1 mmol) in dichloromethane (20 cm^3) was saturated with ammonia gas at 0 °C and then heated to 60 °C in a high pressure tube for 7 days. The tube was cooled in an ice bath before opening and the yellow precipitate which formed was collected by filtration, washed with dichloromethane (3 × 5 cm^3) and ether (10 cm^3) and dried. The hydroiodide salt obtained (0.3 g) was treated with aqueous sodium hydroxide (1.5 mol dm^{-3}, 10 cm^3) and extracted with dichloromethane (4 × 25 cm^3). The organic extract was dried, filtered and evaporated to dryness under reduced pressure to yield the *title compound* as a pale yellow solid (0.11 g, 39%), mp 165–167 °C; ν_{max} (Nujol) 3200 (br), 1609, 1593, 1501, 1179 cm^{-1}; δ_H ($CDCl_3$) 1.55, (2 H, br s, CH_2NH_2), 1.61 (4 H, m, 3,4-CH_2), 1.98 (2H, m, 2-CH_2), 2.80 (2H, m, 5-CH_2), 4.36 (2H, t, *J* 8, ArNCH_2), 7.31 (2H, t, *J* 7.5, 2,7-H), 7.50 (2H, d, *J* 7.5, 4,5-H), 7.74 (2H, dt, *J* 1.5 and 7.5, 3,6-H), 8.59 (2H, dd, *J* 1.5 and 7.5, 1,8-H); δ_C ($CDCl_3$) 24.6, 27.4, 33.6, 42.3, 46.4, 114.6, 121.6, 122.8, 128.4, 134.3, 142.1, 178.4; HRMS (ES^+), found: 281.1651(MH^+); $C_{18}H_{21}N_2O$ requires 281.1654.

Europium(III) sodium salt of *N*-(7-oxo-9,12,15,15-tetracarboxymethyl-6,9,12,15-tetraazapentadecyl)acridone 34. A solution of the amine **32** (75 mg, 0.27 mmol) in anhydrous DMF (4 cm^3) was added to a mixture of diethylenetriaminepentaacetate bisanhydride (0.107 g, 0.27 mmol) and triethylamine (0.14 g, 1.35 mmol) in anhydrous DMF (5 cm^3) under argon. The reaction was stirred overnight, then half of the product was evaporated to dryness under reduced pressure and taken up in aqueous sodium carbonate solution (0.1 mol dm^{-3}, 5 cm^3) and treated with europium(III) chloride hexahydrate (55 mg, 0.15 mmol) and the mixture stirred for 16 h. The precipitate that formed was filtered off and the title compound was precipitated out of solution by the addition of acetone. The precipitate was taken up in the minimum volume of water and then reprecipitated with acetone, to afford the *product salt* as a white powder. This showed red, solid state luminescence

under ultraviolet illumination. The solid (30 mg, 27%) showed mp > 300 °C; λ_{max} (H_2O) 217 (7500), 257 (18000), 394 (2700), 414 (2700); ν_{max} (Nujol) 3366 (br), 1603, 1407, 1094, 933 cm^{-1}; *m*/*z* (FAB) 850 (M + Na^+); HRMS (ES^+), found: 850.1555 (M + Na^+); $C_{32}H_{37}N_5O_{10}{}^{153}EuNa_2$ requires 850.1548.

Formation of europium(III) complexes of the cyclen derivatives. The following general method was used: To a solution of the acid (0.1 mmol) in methanol (1.5 cm^3) was added a solution of europium chloride hexahydrate (0.1 mmol) in methanol (1.5 cm^3) and the solution heated at 50 °C overnight, before concentrating the volume to *ca.* 1 cm^3. Ether was added to the solution dropwise until a slight clouding of the solution began; this was then left in an atmosphere of ether overnight to effect crystallization. The precipitated solid was then collected by filtration and washed thoroughly with ether to afford the appropriate salt. In this manner compounds **27**–**29** were obtained.

The *europium salt* **27** (84%), as a yellow powder, mp > 300 °C; λ_{max} (H_2O) 257 (35000), 394 (5200), 410 (5100); ν_{max} (Nujol) 3341 (br), 1611, 1590, 1270, 1181 cm^{-1}; HRMS (ES^+), found: 760.2224 (MH^+); $C_{32}H_{41}N_5O_7{}^{153}Eu$ requires 760.2218.

The *europium salt* **28** (47%), as a bright yellow solid, mp > 300 °C; *m*/*z* small cluster around 914–920 indicative of the required complex.

The *europium salt* **29** (58%), as a yellow solid, mp > 300 °C; λ_{max} (H_2O) 257 (45000), 394 (6800), 409 (6700); ν_{max} (Nujol) 3352 (br), 1611, 1592, 1290, 1267, 1182 cm^{-1}; *m*/*z* (ES) 718, 716 (MH^+); HRMS (ES^+), found: 718.1748 (MH^+); $C_{29}H_{35}N_5O_7{}^{153}Eu$ requires 718.1749.

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