



HAL
open science

Exploring the luminescent sensing of anions by the use of an urea functionalized 1,10-phenanthroline (phen) based (3:1) Eu(III) complex

Thorfinnur Gunnlaugsson, Cidalia dos Santos

► To cite this version:

Thorfinnur Gunnlaugsson, Cidalia dos Santos. Exploring the luminescent sensing of anions by the use of an urea functionalized 1,10-phenanthroline (phen) based (3:1) Eu(III) complex. *Supramolecular Chemistry*, 2009, 21 (01-02), pp.173-180. <10.1080/10610270802588285>. <hal-00513551>

HAL Id: hal-00513551

<https://hal.science/hal-00513551v1>

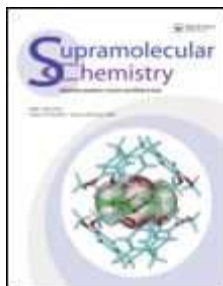
Submitted on 1 Sep 2010

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization



Exploring the luminescent sensing of anions by the use of an urea functionalized 1,10-phenanthroline (phen) based (3:1) Eu(III) complex

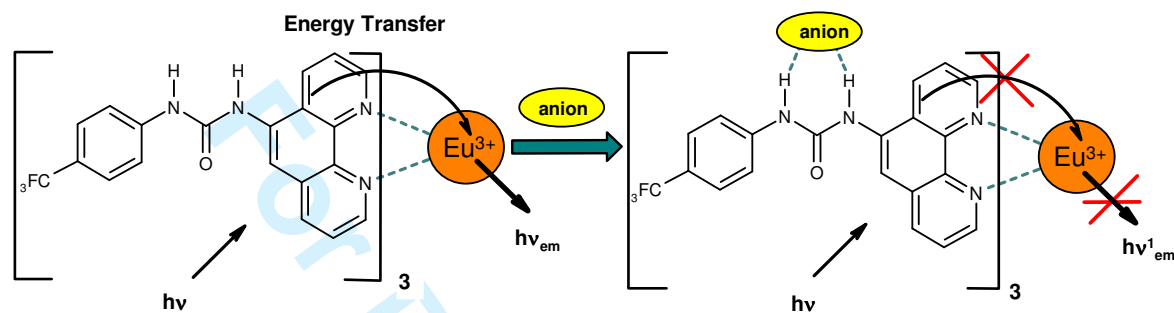
Journal:	<i>Supramolecular Chemistry</i>
Manuscript ID:	GSCH-2008-0126.R2
Manuscript Type:	Special Issue Paper
Date Submitted by the Author:	29-Oct-2008
Complete List of Authors:	Gunnlaugsson, Thorfinnur; Trinity College Dublin, Chemistry dos Santos, cidalia; Trinity College Dublin, Chemistry
Keywords:	anions, sensing, lanthanide, europium, self-assembly



Graphical abstract

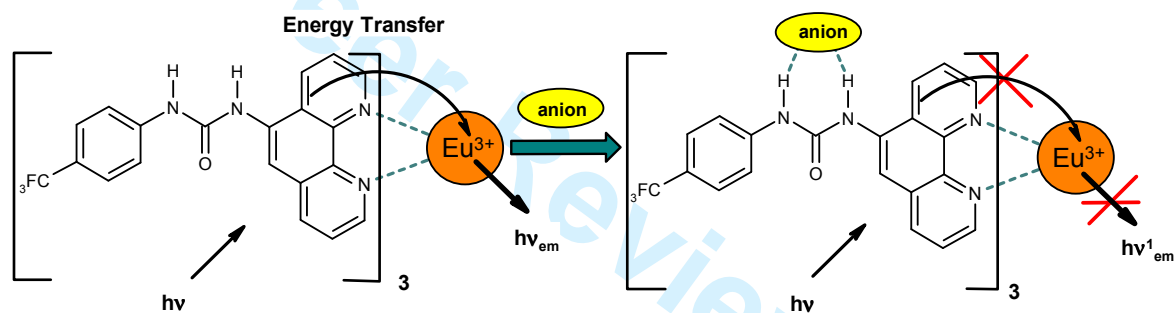
Exploring the luminescent sensing of anions by the use of an urea functionalized 1,10-phenanthroline (phen) based (3:1) Eu(III) complex

Cidália M. G. dos Santos and Thorfinnur Gunnlaugsson



Graphical abstract**Exploring the luminescent sensing of anions by the use of an urea functionalized 1,10-phenanthroline (phen) based (3:1) Eu(III) complex**

Cidália M. G. dos Santos and Thorfinnur Gunnlaugsson



Graphical Abstract

1
2
3 Exploring the luminescent sensing of anions by the use of an urea
4 functionalized 1,10-phenanthroline (*phen*) based (3:1) Eu(III)
5
6 complex
7
8
9

10
11
12 Cidália M. G. dos Santos and Thorfinnur Gunnlaugsson*

13 *School of Chemistry, Centre for Synthesis and Chemical Biology, Trinity College Dublin, Dublin*

14
15
16
17 *2, Ireland. E-mail: gunnlaut@tcd.ie*
18
19
20

21
22 **Abstract:** The design, synthesis and photophysical evaluation of the Eu(III) complex **1₃Eu**,
23 formed from the aryl-urea based 1,10-phenanthroline (*phen*) heteroditopic receptor **1**, is
24 described. The complex, which was formed in 3:1 [ligand:Eu(III)] stoichiometry, was used to
25 sense anions such as acetate, phosphate and halides, in CH₃CN. Here, the mechanism for the
26 sensing of these anions by **1₃Eu** was through hydrogen bonding at the urea moiety, and in the
27 case of F⁻, also by the displacement of metal bound water molecules. Both these binding
28 modes gave rise to significant modulation in spectroscopic output of the Eu(III) complex.
29
30
31
32
33
34
35
36
37
38
39

40 **Keywords:** Anions, sensing, lanthanide, europium, self-assembly, displacement assays.
41
42
43
44

45 INTRODUCTION

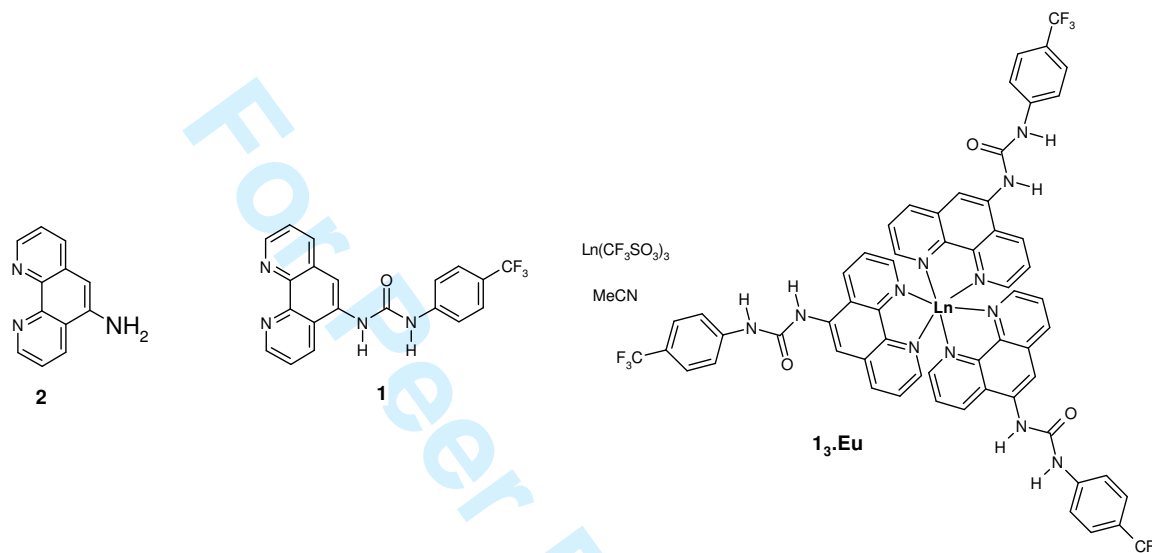
46
47 Over the years, much effort has been devoted to the development of selective sensors
48 for detecting anions.[1-4] In particular, the use hydrogen bonding receptors such as those
49 based on the use of urea/thioureas,[5], pyrroles[6] and indoles,[7] has been extensively
50 researched. At the same time, the use of transition metal ion complexes for binding ions, with
51 subsequent changes in the photo-physical properties of the metal ion complex, has also been a
52 fruitful area of research.[8] More recently, the use of lanthanide ion complexes in anion
53 sensing has also become a fast growing area of research, where the anion sensing occurs via a
54
55
56
57
58
59
60

1
2
3 direct coordination at the metal ion itself.[9-13] In contrast to these developments, then he use
4 of a combination of two modes of binding, e.g. hydrogen bonding donors and metal ion
5 complexes, for anion recognition and sensing has been much less explored, and mostly
6 through the use of transition metal ions.[14] With the aim of developing such sensors for
7 anions using lanthanide ions, we have recently synthesised Tb(III) based cyclen complexes
8 that possess a di-aryl based urea pendant arm.[15] Here the hydrogen donating urea moiety
9 acted as an anion receptor, as well as a sensitizer, or an antenna, for the population of the
10 Tb(III) excited state. In this work, we showed, that the Tb(III) could be sensitized by
11 excitation of the antenna, and that the sensitization process could be modulated upon
12 recognition of several anions such as acetates and phosphates at the urea moiety in non-
13 aqueous solution. We also demonstrated that for this same system, at high concentration,
14 additional anion binding occurred at the lanthanide ion centre directly through the mechanism
15 of displacement of metal bound water molecules [16].
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32

33
34 In this communication, we set out to further explore the use of a combination of
35 hydrogen bonding receptors and the lanthanides for anion sensing, by using acyclic ligands.
36 Here we describe the synthesis and the photophysical evaluation of **1₃Eu**, formed from the
37 *phen* based urea heteroditopic receptors **1** and Eu(III), and we demonstrate that the
38 photophysical properties of **1₃Eu** are significantly modulated upon recognition of anions in
39 organic solvent. While similar ideas have been developed by several other researchers such as
40 Hamilton *et al.*[17], Fabbrizzi *et al.*[18] Branda *et al.*[19] and Steed *et al.*[20], these examples
41 have all been based on the use of transition metal ions, and not lanthanide ions. Hence, the
42 formation of lanthanide complexes, has not, to the best of our knowledge, been achieved to
43 date.
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

RESULTS AND DISCUSSION

Synthesis: The synthesis of **1** was achieved in two steps from the commercially available 5-nitro-1,10-phenanthroline by firstly converting it to the corresponding amine **2** in 92% yield, by using hydrazine monohydrate in the presence of 10% Pd/C catalyst in ethanol at 95°C, followed by reaction with trifluoro-*p*-tolyl isocyanate, in chloroform at room temperature,



Scheme 1. Synthesis of **1** and the Eu(III) complex of **1**, **1₃Eu** (several structural isomers were expected to be formed).

which gave **1** as an off white precipitate, in 88% yield after recrystallization from a mixture of CHCl₃:MeOH,[21] Scheme 1. The synthesis of the Eu(III) complex of **1**, was accomplished by reacting **1** with 0.5 equivalents of Eu(CF₃SO₃)₃ in CH₃CN at room temperature overnight. The observed off white precipitate was isolated by filtration, and dried under vacuum to produce a bright yellow solid in a modest 28% yield. The successful synthesis of **1₃Eu** was supported by NMR spectroscopy and HRMS. Although the ¹H NMR was not greatly shifted (due to the presence of the paramagnetic Eu(III) ion), the formation of **1₃Eu** complex was clear in the ¹H NMR, which showed significant broadening for the *phen* protons, indicating the presence of a single species in solution possessing high symmetry. The ¹⁹F spectrum also revealed the presence of the CF₃ group at -60.56 ppm as well as a resonance at -78.29 ppm which we assigned to the triflate counter ions. The ESMS also showed the expected europium

isotopic distribution pattern for ${}^1_3\text{Eu}$, for instance for the m/z centred at 647 assigned to the $[\text{M}/2]$ peak.

Photophysical studies: The formation and the stability of the complex between Eu(III) and **1**, was investigated by observing the changes in the ground and the singlet excited state of **1** (10 μM), and the Eu(III) emission upon titration with $\text{Eu}(\text{CF}_3\text{SO}_3)_3$ in CH_3CN under ambient conditions. The changes observed in the absorption spectra of **1**, which had a λ_{max} of 265 nm and a shoulder at 320 nm, are shown in Figure 1.

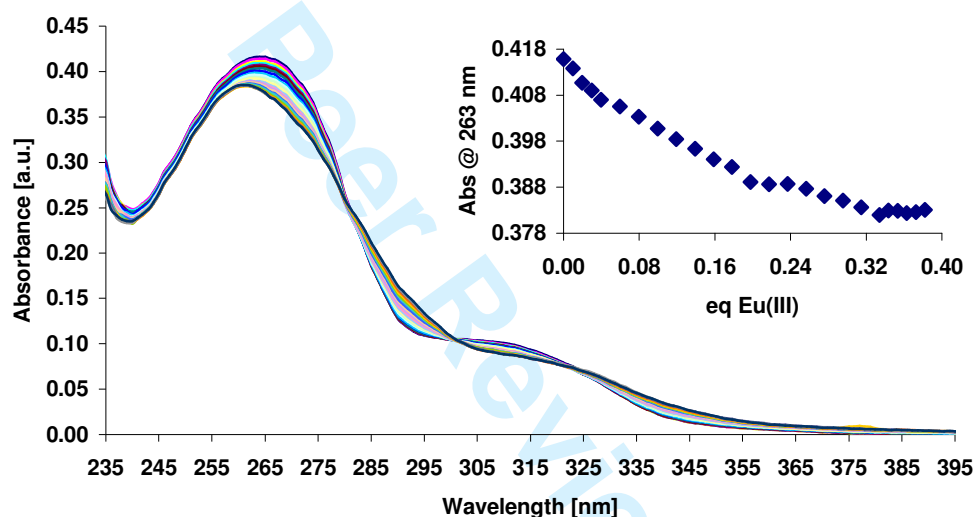


Figure 1. Changes on the absorption spectra of **1** (10 μM) upon addition of $\text{Eu}(\text{CF}_3\text{SO}_3)_3$.
Insert: The changes in absorbance at 263 nm as a function of equivalents of Eu(III).

Upon binding to Eu(III), small shifts were observed in the absorption spectra, where the 265 nm band was blue shifted to 260 nm, and the 320 nm shoulder was concomitantly red shift by ca. 5 nm. Three distinct isosbestic points were also observed at 280 nm, 300 nm, and 323 nm, respectively. The titration profile for the changes at 253 nm is also shown as an insert in Figure 1, which demonstrated the formation of a complex with 1:3 stoichiometry (e.g. ${}^1_3\text{Eu}$) as no significant changes occurred after ca. 0.33 eq. of Eu(III) added. The homogenous changes in the absorption spectra also demonstrate that the complex does not aggregate in solution.

The changes in the fluorescence emission were also monitored upon excitation at 265 nm and 320 nm. On both occasions, a broad band centred at 422 nm was observed. Upon addition of Eu(III), the emission intensity arising from this transition was quenched by 33%, without any changes in λ_{max} . By plotting the changes in the emission intensity at 422 nm versus equivalents of Eu(III), in a similar manner to that described above, again demonstrates the formation of the desired 1:3 stoichiometry in solution.

The formation of this complex was also clearly evident from the changes in the Eu(III) emission, Figure 2, which shows the formation of new bands centred at 594, 616, 652, and 700 nm, corresponding to the deactivation of the Eu(III) 5D_0 excited state to the 7F_J ground states ($^5D_0 \rightarrow ^7F_J$, $J = 1-4$), respectively. These results confirm that the *phen* ligand is capable

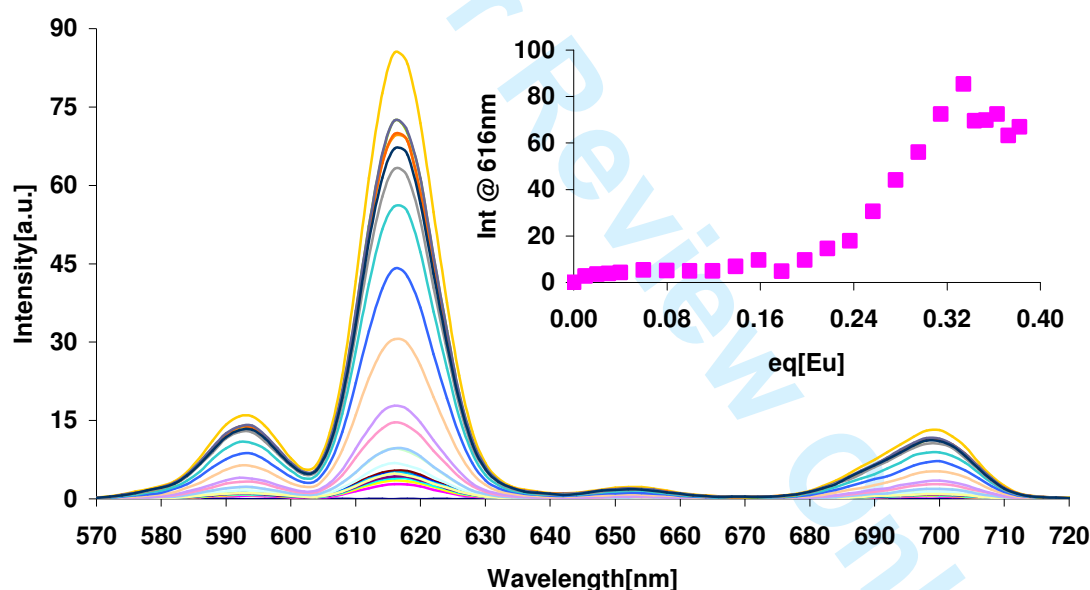


Figure 2. Changes on the Eu(III) emission of **1** (10 μM), which is enhanced upon addition of Eu(CF₃SO₃)₃. *Insert:* The changes in lanthanide emission at 616 nm as a function of equivalents of Eu(III) added, upon excitation at 265 nm.

of successfully sensitize the Eu(III) excited state. Furthermore, as can be seen in Figure 2, the $J = 2$ band, occurring at 616 nm, gave rise to large changes in the Eu(III) emission upon formation of **1₃Eu**. This transition is highly sensitive to its coordination environment, so these results are indicative of direct coordination between the *phen* ligand and the Eu(III) ion.

Analysis of the changes in the $J = 2$, shown as inset in Figure 2, demonstrate the formation of the desired 1:3 complex, and its formation was further confirmed by using Job's plot analysis ($m/n = f_{\max} / (1 - f_{\max})$), gave $f_{\max} = 0.25$, and $m/n = 1/3$, for the changes in the 616 nm band.

The luminescence changes observed in Figure 2, were also analysed by fitting the data using the nonlinear least-squares fitting program SPECFIT. The results of this fitting are shown in Table 1, and demonstrate the stepwise formation of **1Eu**, **1₂Eu**, and **1₃Eu** complexes in solution, and that the **1₃Eu** complex is formed with $\log K_{1:3}$ of ~ 6 . Similar analysis was carried out on the changes observed in both the ground and the singlet excited state spectrum. On all occasions, the stepwise formation of **1₃Eu** was also observed, Table 1 (expressed as $\log \beta$) where a good correlation was observed between all three spectroscopic techniques.

Table 1. Binding constants and binding modes between Eu(III) and **1**, obtained upon fitting the changes in the absorption, the fluorescence and the Eu(III) emission.

Technique	Species (Eu _n :1 _m)	Log β	Std. Deviation
<i>Absorbance</i>	Eu1	3.86	0.012
	Eu1₂	7.54	0.016
	Eu1₃	13.46	0.031
<i>Fluorescence</i>	Eu1	3.88	0.008
	Eu1₂	7.48	0.016
	Eu1₃	13.38	0.024
<i>Phosphorescence</i>	Eu1	3.61	0.011
	Eu1₂	7.28	0.016
	Eu1₃	13.30	0.017

From Table 1, it is clear that the 1:3 stoichiometry dominates in solution, and hence the Eu(III) ion would be expected to be hexa-coordinated. The overall coordination number of **1₃Eu** was further confirmed, by measuring the hydration state (q), or the number of metal bound water molecules associated with the **1₃Eu** structure, by measuring the excited state lifetimes for the Eu(III) emission in H₂O and D₂O, respectively, by direct excitation of the Eu(III) centre at 395 nm. This gave values of 0.333ms and 1.83 ms for $\tau_{\text{H}_2\text{O}}$ and $\tau_{\text{D}_2\text{O}}$, respectively, which translates, using the Horrocks's modified equation [22] developed by

Parker *et al.*,[23], in to a q value of 2.6, confirming the overall coordination number of $\mathbf{1}_3\mathbf{Eu}$ as nine in aqueous solution.

Anion Sensing: Having successfully synthesised and, analysed the formation of $\mathbf{1}_3\mathbf{Eu}$ in solution, we next investigated its ability to bind/recognize anions. As $\mathbf{1}_3\mathbf{Eu}$ has three urea based ligands, all of which are capable of participating in the recognition of anions through hydrogen bonding, we expected to see significant changes in the photophysical properties of the complex upon such binding. Moreover, and as demonstrated above, the complex has three metal bound solvent molecules, all of which could be displaced by other competitive coordinating ligands, such as anions, with concomitant changes in the coordination environment of the lanthanide ion and hence, in its photophysical properties. Hence, the anion sensing ability of $\mathbf{1}_3\mathbf{Eu}$ could occur through either of these modes, or through the combination of both.

All of the three spectroscopic techniques discussed above were used to monitor the recognition of anions by $\mathbf{1}_3\mathbf{Eu}$ such as acetate, dihydrogenphosphate, fluoride and chloride as their tetrabutylammonium salts (TBA^+), in CH_3CN . Upon titrating AcO^- , the absorption spectrum was significantly affected as demonstrated in Figure 3. These changes were

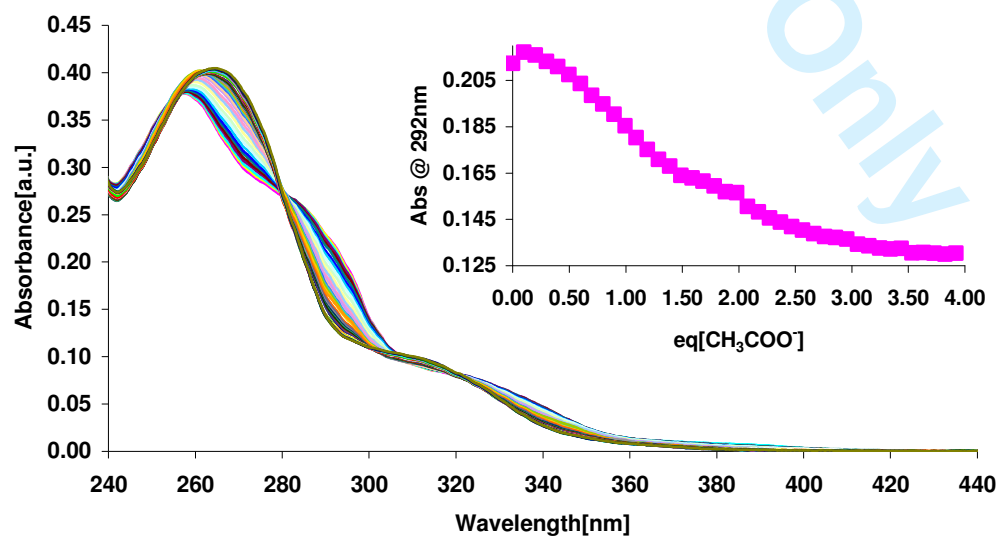


Figure 3. Changes on the absorbance of $\mathbf{1}_3\mathbf{Eu}$ ($4 \mu\text{M}$) upon addition of AcO^- . *Insert:* shows changes in absorbance at 292 nm as a function of equivalents of acetate added.

1
2
3 accompanied by the formation of four isosbestic points at 256, 280, 303 and 322 nm, which
4
5 were attributed to the interaction of the anion with the three urea moieties. Analysis of the
6
7 changes in the absorption spectrum is shown as an inset in Figure 3, and demonstrated that
8
9 these changes occurred up to ca. three equivalents of AcO^- , signifying the formation of
10
11 hydrogen bonding complexes between these anion and the urea moieties. Fitting this data
12
13 using SPECFIT, however, only gave accurate binding constants for two of these binding
14
15 events, namely the 1:1 and the 2:1 (ion:complex) between $\mathbf{1}_3\mathbf{Eu}$ and AcO^- , with binding
16
17 constants $\text{Log } K_{1:1}$ and $\text{Log } K_{2:1}$ of 6.23 (± 0.257) and 6.17 (± 0.169), respectively for these
18
19 interactions. Similar changes were also observed in the absorption spectrum of $\mathbf{1}_3\mathbf{Eu}$ for the
20
21 titration of H_2PO_4^- and F^- . As in the case of AcO^- , then for F^- we were only able to fit the
22
23 spectral changes of two binding events. However, for H_2PO_4^- , the best fits were observed only
24
25 when the data was fitted to binding events which involved the 1:1 and 1:2, complex formation
26
27 as well as the 2:1 and 2:2 complex between $\mathbf{1}_3\mathbf{Eu}$ and H_2PO_4^- . In contrast to these results, the
28
29 titration of Cl^- , Br^- and I^- , gave only rise to the formation of 1:1 complexes. In the case of Cl^-
30
31 and Br^- , the changes in the absorption spectra of $\mathbf{1}_3\mathbf{Eu}$ were of similar nature, at the same time
32
33 as being overall smaller to that observed above. However, in the case of I^- only absorption
34
35 enhancements were observed without the formation of clear isosbestic points.
36
37
38
39
40
41
42

43 The fluorescence emission of $\mathbf{1}_3\mathbf{Eu}$ was also affected upon carrying out anion
44
45 titrations. After excitation at either 260 nm or 330 nm, fluorescence enhancements of 62%,
46
47 58%, 34%, 10%, and 16% were observed for AcO^- , F^- , Cl^- , Br^- , and I^- , respectively, with no
48
49 apparent shifts in the 420 nm band. These changes were analysed in the same manner as
50
51 described above for the ground state changes. As an example, then in the case of AcO^- ,
52
53 plotting the changes as a function of added equivalents, clearly showed that the changes occur
54
55 up to the binding of three equivalents of AcO^- , indicative of the 3:1 binding stoichiometry.
56
57
58
59
60 However, in the case of H_2PO_4^- , initial quenching was also observed of ca. 15%.

Nevertheless, after the addition of 0.5 equivalents of H_2PO_4^- , the emission was enhanced in a similar manner to that observed above.

However, from these spectroscopic anion titrations, the most significant changes were observed in the Eu(III) emission of $\mathbf{1}_3\text{Eu}$, which was quenched up to *ca.* 2 equivalents of AcO^- (after initial slight enhancement $\sim 3\%$), Figure 4. The insert in Figure 4, also shows the

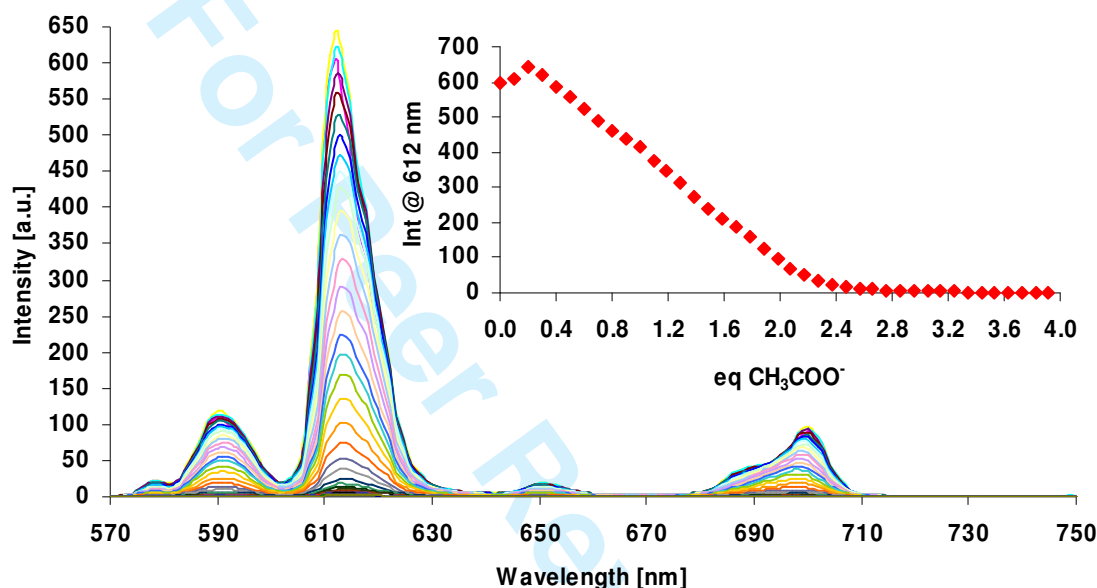


Figure 4. Changes on the lanthanide emission intensity of $\mathbf{1}_3\text{Eu}$ ($4 \mu\text{M}$), which was quenched upon titration with AcO^- . Insert shows changes in intensity at 612 nm as a function of added equivalents of AcO^- .

profile of the changes in luminescence intensity at 612 nm ($J = 2$ band) as a function of the number of equivalents of AcO^- added, and in a similar manner to that observed for the UV-Visible and fluorescence titrations above, demonstrates that two equivalents of AcO^- were needed to fully quench the lanthanide emission. We propose that this quenching can be attributed to an energy mismatch between the lowest triplet state (T_1) of the antenna and the excited state of europium, hence making the transfer of energy unfavourable from the triplet state of the antenna, T_1 , to the excited state of the Eu(III), $^5\text{D}_0$, upon anion recognition. Alternatively it is also possible that some contribution from dissociation, or displacement of $\mathbf{1}$ from the Eu(III) centre in $\mathbf{1}_3\text{Eu}$ could occur upon formation of hydrogen bonding complex

1
2
3 between the urea and the anions, however to date we have been unable to fully quantify if
4 such displacement is occurring. With the aim of evaluating these binding modes of the anion,
5 analysis of the changes seen in Figure 4 were undertaken using SPECFIT. As had been
6 observed for the changes in the ground state, the fitting of the changes observed in the AcO^- ,
7 showed that the 1:1 and the 2:1 stoichiometries were the most dominating, with $\text{Log } K_{1:1}$ and
8 $\text{Log } K_{2:1}$, of $6.56 (\pm 0.118)$ and $7.0 (\pm 0.061)$, which are in agreement with those values
9 observed from the ground and the singlet state changes. In a similar manner, H_2PO_4^- also gave
10 rise to luminescent quenching. However, these changes were best fitted using a variety of
11 binding equilibria such as 1:1, 1:2, 2:1 and 2:2, which would indicate that the anion bound
12 to ${}^3\text{Eu}$ in a more complicated manner than AcO^- . However, for both of these anions, the
13 main binding seems to be through hydrogen bonding at the urea moieties, with lesser
14 contribution from direct binding to the lanthanide centre, via the displacement of metal bound
15 solvent molecules.

16
17 However, such binding combination was observed for the titration of ${}^3\text{Eu}$ using F^- ,
18 Figure 5, where the Eu(III) emission was initially significantly enhanced up to ca. one

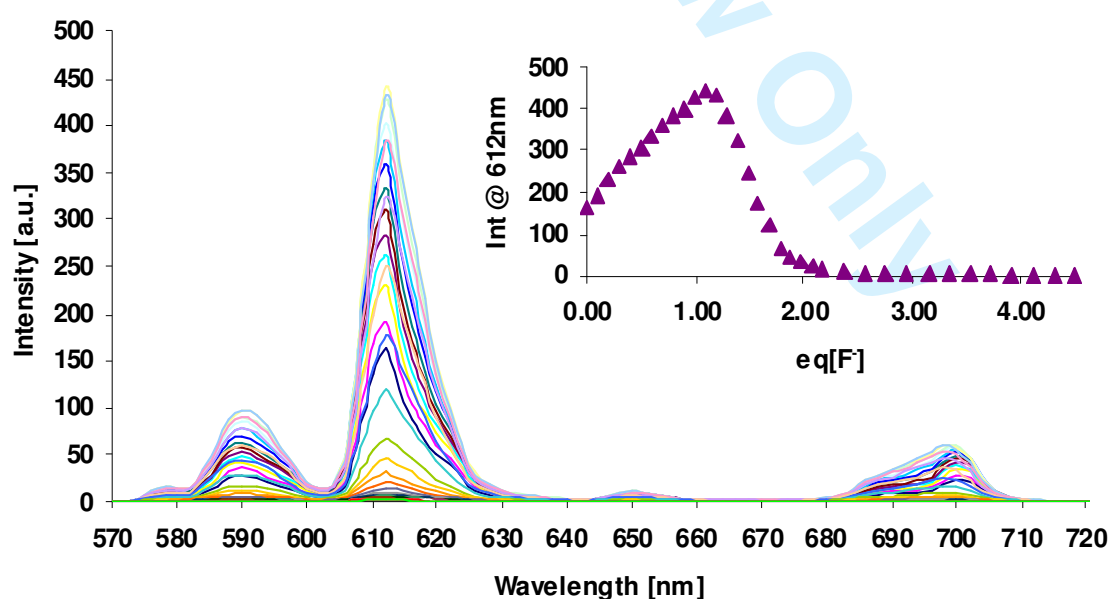


Figure 5. The overall changes on the Eu(III) emission of $\text{Eu}:\mathbf{1}_3$ (4 μM) upon addition of F^- .
Insert: The changes in the intensity at 612 nm as a function of added equivalents of F^- .

1
2
3 equivalent of the ion, which we propose is due to the displacement of a metal bound solvent
4 molecule by F^- . However, these changes were subsequently followed by almost complete
5 quenching in the Eu(III) emission, as demonstrated in the insert in Figure 5 for the changes in
6 the 612 nm transition, in a similar manner to that observed for AcO^- above. This second
7 binding, we assign to the recognition of the anion at the urea site. From these luminescence
8 changes, analysis, using SPECFIT, gave good fitting of the experimental data, from which we
9 were able to obtain two binding constants, log K of 10.35 and 8.2 for the 1:1 and 1:2 bindings,
10 respectively. These are significantly higher binding values than observed for AcO^- or $H_2PO_4^-$,
11 respectively, which might further support the different mode of binding experienced by F^- . In
12 contrast to these results, the titration with Cl^- , Br^- and F^- , only gave rise to 1:1 binding, with
13 binding constant, $LogK_{1:1}$ of 6.34, 6.18, and 6.26, being determined for these anions,
14 respectively. From these results we have established, that only for F^- is the emission
15 enhanced, which demonstrates that the initial anion binding is caused by the binding of the
16 anion at the metal ion centre and that the second equivalent of the anion, binds to the complex
17 via hydrogen bonding interactions at the urea site, which gives rise to quenching in the Eu(III)
18 emission, as the efficiency of the sensitisation process is altered upon anion binding. Such
19 binding interactions were also observed for the other anions investigated herein. We are
20 currently in the process of evaluating these binding modes in greater detail as well as
21 developing analogue systems which possess higher Eu(III) binding affinities and
22 consequently could give rise to the sensing of anions by using such heteroditopic receptors
23 and lanthanide luminescence in a more competitive aqueous environment.
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54

55 CONCLUSION

56
57 In this communication, we have described the synthesis and the characterisation of a new
58 lanthanide complex between an urea based heteroditopic *phen* receptor and Eu(III). We
59
60

1
2
3 demonstrate, using ground, single excited and phosphorescence spectroscopy, that the
4
5 resulting complex is formed in 3:1 (ligand to metal ion) stoichiometry, and that this complex
6
7 can interact with anions in CH₃CN. In particular, in the case of AcO⁻, H₂PO₄⁻, Cl⁻, Br⁻, and
8
9 I⁻, the titration of these ions lead to significant changes in the Eu(III) emission, which was
10
11 fully quenched, in the case of AcO⁻, H₂PO₄⁻, within the addition of 3 equivalents of these
12
13 anions. This we propose as being the result of binding of these anions at the urea moieties in
14
15 **1₃Eu**. In contrast, the titration of F⁻, gave rise to initial enhancement in the Eu(III) emission
16
17 up to one equivalent, followed by luminescence quenching. This we assign to dual binding
18
19 modes involving initial binding of the anion at the metal ion centre itself, with concomitant
20
21 removal one solvent molecule, and enhancement in the Eu(III) emission, followed by
22
23 quenching in the Eu(III) emission upon binding of the anion at one or more of the urea
24
25 moieties in **1₃Eu**.
26
27
28
29
30
31
32
33

34 **ACKNOWLEDGMENTS**

35
36 We thank Trinity College Dublin, CSCB, SFI and IRCSET for financial support. We also like
37
38 to thank Dr. John E. O'Brien for his help.
39
40
41
42

43 **EXPERIMENTAL**

44
45 **General:** Reagents (obtained from Aldrich) and solvents were purified using standard
46
47 techniques. Melting points were determined using a Gallenkamp melting point apparatus.
48
49 Infrared spectra were recorded on a Mattson Genesis II FTIR spectrophotometer equipped
50
51 with a Gateway 2000 4DX2-66 workstation. ¹H NMR spectra were recorded at 400 MHz
52
53 using a Bruker Spectrospin DPX-400 instrument. ¹³C NMR spectra were recorded at 100
54
55 MHz using a Bruker Spectrospin DPX-400 instrument.
56
57
58
59
60

1
2
3 **1-[1,10]Phenanthroline-5-yl-3-(4-trifluoromethyl-phenyl)-urea (1):** To a suspension of the
4
5 amine (3) (1.0 g, 5.12 mmol) in CHCl₃ (40 mL) trifluoro-p-tolyl isocyanate (0.79 mL, 5.63
6
7 mmol) was added. After five minutes all the amine was dissolved, and a dark yellow solution
8
9 was observed. The reaction mixture was stirred overnight at room temperature, under an
10
11 argon atmosphere. An off white precipitate was observed on the reaction vessel. This
12
13 precipitate was filtered and washed with cold CHCl₃. The obtained solid was recrystallized
14
15 from MeOH to yield a pale solid (1.38 g, 88% yield). m.p. decomposes above 290°C;
16
17 Calculated for C₂₀H₁₄N₄OF₃ $m/z = 383.1120$ [M + H]. Found $m/z = 383.1107$. ¹H NMR (400
18
19 MHz, *d*₆-(CD₃)₂SO, δ_H): 9.55 (br s, 1H, NH), 9.16 (d, 1H, *phen*-CH, *J* = 4.0 Hz), 9.12 (br s,
20
21 1H, NH), 9.00 (d, 1H, *phen*-CH, *J* = 4.0 Hz), 8.65 (d, 1H, *phen*-CH, *J* = 8.5 Hz), 8.43 (d, 1H,
22
23 *phen*-CH, *J* = 8.0 Hz), 8.39 (s, 1H, *phen*-CH), 7.89 (dd, 1H, *phen*-CH, *J* = 4.0 Hz), 7.72 (m,
24
25 5H, *phen*-CH + Ar-CH); ¹³C NMR (100 MHz, *d*₆-(CD₃)₂SO, δ_C): 152.87, 149.87, 148.74,
26
27 145.89, 143.34, 143.13, 135.61, 132.08, 130.44, 128.50, 126.25, 126.22, 123.77, 123.68,
28
29 122.95, 122.21, 118.01, 116.07; ¹⁹F NMR (376 MHz, *d*₆-(CD₃)₂SO, δ_F): -60.58 (CF₃); MS
30
31 (ES⁺) $m/z = 383.11$ (M + H). IR ν_{max} (cm⁻¹) 3394, 3284, 3211, 3089, 1711, 1613, 1563, 1505,
32
33 1472, 1411, 1377, 1329, 1310, 1270, 1202, 1162, 1153, 1108, 1097, 1066, 1017, 988, 945,
34
35 878, 848, 826, 803, 737, 711, 691.

36
37 **Europium complex of 1, 1₃Eu:** To a suspension of the urea (1) (0.10 g, 0.26 mmol) in
38
39 CH₃CN (20 mL) was added Eu(CF₃SO₃)₃ (0.06 g, 0.11 mmol). Within few minutes a clear
40
41 yellow solution was observed. The reaction mixture was stirred overnight, at room
42
43 temperature under an argon atmosphere. The precipitate was isolated by filtration, and dried
44
45 under vacuum to produce a bright yellow solid in (0.13 g, 28% yield). ¹H NMR (600 MHz,
46
47 *d*₆-(CD₃)₂SO, δ_H): 9.52 (s, 1H, NH), 9.15 (br s, 1H, *phen*-CH), 9.10 (s, 1H, NH), 8.98 (br s,
48
49 1H, *phen*-CH), 8.64 (d, 1H, *phen*-CH, *J* = 8.6 Hz), 8.43 (d, 1H, *phen*-CH, *J* = 7.6 Hz), 8.35 (s,
50
51 1H, *phen*-CH), 7.88 (br s, 1H, *phen*-CH), 7.74 (d, 2H, Ar-CH, *J* = 8.6 Hz), 7.70 (br s, 1H,
52
53
54
55
56
57
58
59
60

1
2
3 *phen*-CH), 7.69 (d, 2H, Ar-CH, $J = 8.6$ Hz); ^{19}F NMR (376 MHz, d_6 -(CD_3) $_2\text{SO}$, δ_{F}): -60.56
4
5 (CF $_3$), -78.29 (CF $_3\text{SO}_3$); MS (ES $^+$) $m/z = 558.00$ [(M-2*phen* ligands) + Na] 648.95 [M/2],
6
7 684.91 [(M/2) + 2H $_2\text{O}$].; IR ν_{max} (cm $^{-1}$) 3334, 1656, 1605, 1542, 1412, 1314, 1223, 1160,
8
9 1107, 1066, 1026, 844, 808, 733, 719, 695.

References:

- 10
11
12
13
14
15
16
17 [1] Sessler, J. L.; Gale, P. A.; Cho, W. S., *Anion Receptor Chemistry*; Royal Society of
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
- [1] Sessler, J. L.; Gale, P. A.; Cho, W. S., *Anion Receptor Chemistry*; Royal Society of
Chemistry: Cambridge, UK, 2006.
- [2] Gunnlaugsson, T.; Glynn, M.; Tocci (née Hussey), G. M.; Kruger, P. E.; Pfeffer, F. M.
Coord. Chem. Rev., **2006**, *250*, 3094; Gunnlaugsson, T.; Ali H.D.P.; Glynn, M.; Kruger, P.E.;
Hussey G. M. Pfeffer F. M.; dos Santos, C. M. G.; Tierney, J.; *J. of. Fluoresc.*, **2005**, *15*,
287. Gunnlaugsson, T.; Leonard J.P. *Chem. Commun.* **2005**, 3114; Leonard J.P.;
Gunnlaugsson T. *J. of. Fluoresc.* **2005**, *15*, 585.
- [3] Steed, J. W., *Chem. Commun.*, **2006**, 2637; Martínez-Mañez, R. Sancenón, F. *Chem. Rev.*,
2003, *103*, 4419. Suksai, C.; Tuntulani, T. *Chem. Soc. Rev.*, **2003**, *32*, 192 J. F. Callan, A.P.
de Silva, D.C. Magri, *Tetrahedron*, **2005**, *36*, 8551; deSilva, A.P.; Gunaratne, H.Q.N.;
Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher J. T.; Rice, T. E. *Chem. Rev.*
1997, *97*, 1515.
- [4] Gale, P. A., *Acc. Chem. Res.*, **2006**, *39*, 465. Gale P. A. *Chem. Commun.*, **2005**, 3761;
Gale, P.A. *Coord. Chem. Rev.*, **2001**, *213*, 79; Gale, P.A. *Coord. Chem. Rev.*, **2000**, *199*, 181.
- [5] Quinlan E.; Matthews S. E.; Gunnlaugsson, T., *Tetrahedron Lett.*, **2006**, *47*, 9333;
Palacios, M. A.; Nishiyabu, R.; Marquez, M.; Anzenbacher, Jr., P. *J. Am. Chem. Soc.*, **2007**,
129, 7538; Gómez D. E., Fabbrizzi, L., Licchelli, M., Monzani, E. *Org. Biomol. Chem.*, **2005**,
3, 1495; Pfeffer F. M.; Buschgens, A. M.; Barnett, N. W.; Gunnlaugsson, T.; Kruger, P. E.,
Tetrahedron Lett., **2005**, *46*, 6579; Pfeffer, F. M.; Gunnlaugsson, T.; Jensen, P.; Kruger, P.E.,

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Org. Lett. **2005**, 7, 5375; Gunnlaugsson, T.; Kruger, P. E.; Lee, T. C.; Parkesh, R.; Pfeffer, F. M.; Hussey, G. M.; *Tetrahedron Lett.*, **2003**, 44, 6575; Gunnlaugsson, T.; Davis, A.P.; Glynn, M. *Chem. Commun.*, **2001**, 2556.

[6] Katayev, E. A.; Sessler, J. L.; Khrustalev, V. N.; Ustynyuk, Y. A. *J. Org. Chem.* **2007**, 72, 7244; Evans, L. S.; Gale, P. A.; Light, M. E. Quesada, R. *Org. Biomol. Chem.*, **2006**, 4, 1019.

[7] Pfeffer, F. M.; Lim K. F.; Sedgwick, K. J. *Org. Biomol. Chem.*, **2007**, 5, 1795; Bates, G. W.; Triyanti, Light, M. E.; Albrecht, M.; Gale, P. A. *J. Org. Chem.*, **2007**, 72, 8921.

[8] Fabbrizzi, L.; Licchelli, M.; Rabaioli, G.; Taglietti, A. F. *Coord. Chem. Rev.* **2000**, 205, 85.

[9] Leonard, J. P.; Nolan, C. B. Stomeo F.; Gunnlaugsson, T. *Top. Curr. Chem.*, **2007**, 281, 1; Gunnlaugsson T.; F. Stomeo, *Org. Biomol. Chem.*, **2007**, 5, 1999; Pope, S. J. A. *Polyhedron*, **2007**, 26, 4818; Pandya, S.; Yu, J.; Parker, D. *Dalton Trans.* **2006**, 2757; Shinoda, S.; Miyake, H.; Tsukube, H. *Handbook of the Physics and Chemistry of Rare Earths*; Elsevier North Holland, 2005; Vol. 35; Tsukube, H.; Shinoda, S.; *Chem. Rev.*, **2002**, 102, 2389; Parker, D. *Chem. Soc. Rev.*, **2004**, 33 156 Gunnlaugsson, T.; Harte, A. J.; Leonard, J. P.; Nieuwenhuyzen, M. *Chem. Commun.* **2002**, 2134.

[10] Poole, R. A. Kielar, F.; Richardson, S. L.; Stenson, P. S.; Parker D. *Chem. Commun.*, **2006**, 4084; Parker, D. Dickins, R. S. Puschmann, H.; Cossland C.; Howard, J. A. K. *Chem. Rev.* **2002**, 102, 1977.

[11] Plush, S.E; Gunnlaugsson, T. *Dalton Trans.*, **2008**, 3801.

[13] S Plush, S.E; Gunnlaugsson, T. *Org. Lett.*, **2007**, 9, 1919.

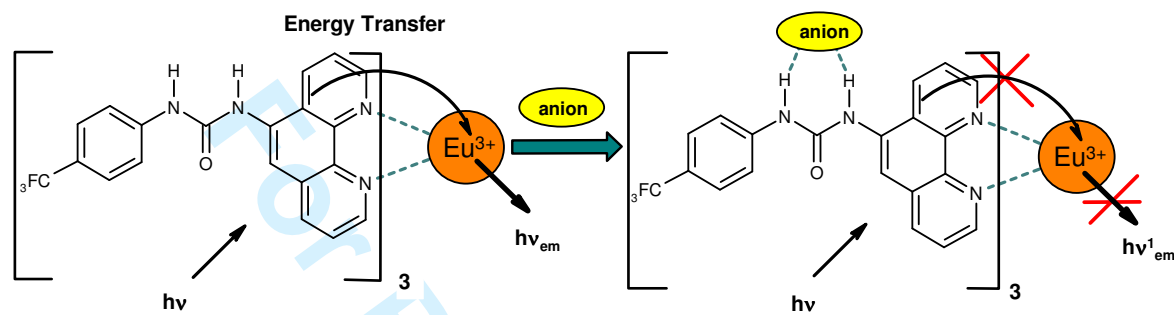
[14] Lankshear, M. D.; Cowley, A. R.; Beer, P. D. *Chem. Commun.* **2006**, 612; Tozawa, T.; Misawa, Y.; Tokita, S.; Kubo, Y. *Tetrahedron Lett.*, **2000**, 41, 5219; Kirkovits, G. J.; Shriver, J. A.; Gale, P. A.; Sessler, J. L. *Journal of Inclusion Phenomena and Macrocyclic Chemistry* **2001**, 41, 69-75; Reetz, M. T. In *Comprehensive Supramolecular Chemistry*; Atwood, L.,

- 1
2
3 Davies, J. E. D., MacNicol, D. D., Vogtle, F., Eds.; Pergamon: Oxford, 1996; Vol. 2, pp 553-
4 562; 7; Beer, P. D.; Timoshenko, V. Maestri, M.; Passaniti P.; Balzani, V. *Chem. Commun.*,
5
6 **1999**, 1755; Beer; P.D. *Chem. Commun.*, **1996**, 689.
7
8
9
10 [15] dos Santos, C. M. G.; Fernandez, P. B.; Plush, S. E.; Leonard, J. P.; Gunnlaugsson, T.
11
12 *Chem. Commun.*, **2007**, 3389.
13
14
15 [16] Gunnlaugsson, T.; Harte, A. J.; Leonard, J. P.; Nieuwenhuyzen, M. *Supramol. Chem.*
16
17 2003, 15, 505; Faulkner S.; Burton-Pye, B. P.; Khan, T.; Martin L. R.; Wray, S. D.; Sakabara,
18
19 P. J. *Chem. Commun.* **2002**, 1668; Dickins, R. S.; Gunnlaugsson, T.; Parker, D.; Peacock, R.
20
21 D. *Chem. Commun.* 1998, 1643.
22
23
24 [17] Goodman, M. S.; Weiss, J.; Hamilton, A. D. *Tetrahedron Lett.* **1994**, 35, 8943.
25
26
27 [18] Amendola, V.; Boiocchi, M.; Colasson, B.; Fabbrizzi, L. *Inorg. Chem.* **2006**, 45, 6138.
28
29
30 [19] Norsten, T. B.; Chichak, K.; Branda, N. R. *Chem. Commun.* **2001**, 1794.
31
32 [20] Turner, D. R.; Spencer, E. C.; Howard, J. A. K.; Tocher, D. A.; Steed, J. W. *Chem.*
33
34 *Commun.* **2004**, 1352; Turner, D. R.; Smith, B.; Spencer, E. C.; Goeta, A. E.; Evans, I. R.;
35
36 Tocher, D. A.; Howard, J. A.; Steed, J. W. *New J. Chem.* **2005**, 29, 90.
37
38
39 [21] dos Santos, C. M. G.; McCabe T.; Gunnlaugsson, T. *Tetrahedron Lett.*, **2007**, 48, 3135.
40
41
42 [22] Supkowski, R. M.; Horrocks, W. D. *Inorg. Chem. Acta.*, **2002**, 340, 44.
43
44 [23] Beeby, A.; Clarkson, I. M.; Dickens, R. S.; Faulkner, S.; Parker, D.; Royle, L.; de Sousa,
45
46 A.S.; Williams, J.A.G.; Woods, M. J. *Chem. Soc, Perkin Trans.*, 2, **1999**, 493.
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Graphical abstract

Exploring the luminescent sensing of anions by the use of an urea functionalized 1,10-phenanthroline (phen) based (3:1) Eu(III) complex

Cidália M. G. dos Santos and Thorfinnur Gunnlaugsson



1
2
3 Exploring the luminescent sensing of anions by the use of an urea
4 functionalized 1,10-phenanthroline (*phen*) based (3:1) Eu(III)
5
6
7
8 complex
9
10

11
12 Cidália M. G. dos Santos and Thorfinnur Gunnlaugsson*

13 *School of Chemistry, Centre for Synthesis and Chemical Biology, Trinity College Dublin, Dublin*

14
15 *2, Ireland. E-mail: gunnlaut@tcd.ie*
16
17
18
19
20

21 **Abstract:** The design, synthesis and photophysical evaluation of the Eu(III) complex **1₃Eu**,
22 formed from the aryl-urea based 1,10-phenanthroline (*phen*) heteroditopic receptor **1**, is
23 described. The complex, which was formed in 3:1 [ligand:Eu(III)] stoichiometry, was used to
24 sense anions such as acetate, phosphate and halides, in CH₃CN. Here, the mechanism for the
25 sensing of these anions by **1₃Eu** was through hydrogen bonding at the urea moiety, and in the
26 case of F⁻, also by the displacement of metal bound water molecules. Both these binding
27 modes gave rise to significant modulation in spectroscopic output of the Eu(III) complex.
28
29
30
31
32
33
34
35
36
37
38
39

40 **Keywords:** Anions, sensing, lanthanide, europium, self-assembly, displacement assays.
41
42
43
44

45 INTRODUCTION

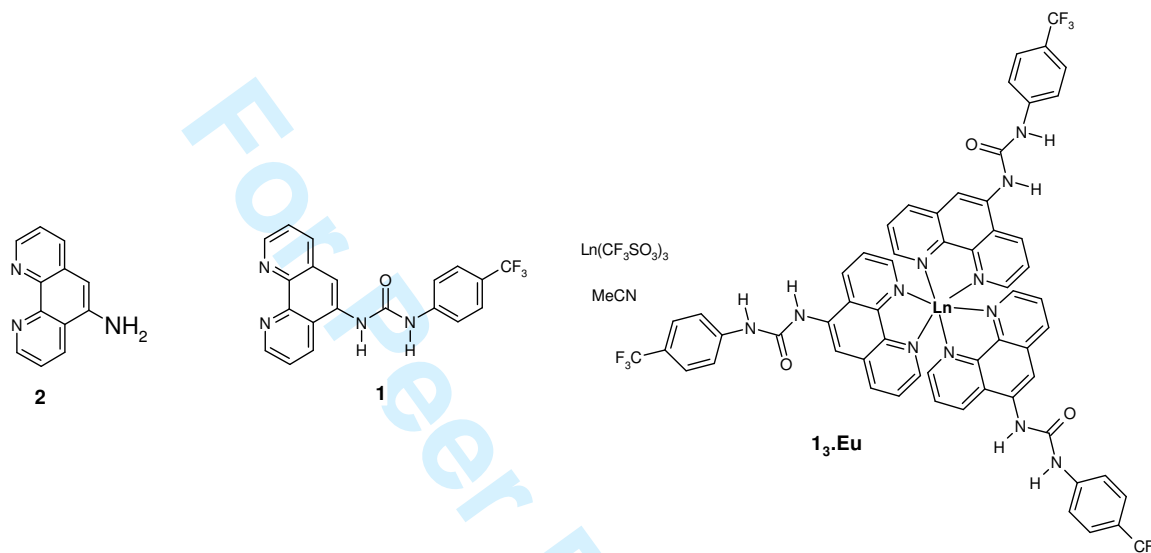
46
47 Over the years, much effort has been devoted to the development of selective sensors
48 for detecting anions.[1-4] In particular, the use hydrogen bonding receptors such as those
49 based on the use of urea/thioureas,[5], pyrroles[6] and indoles,[7] has been extensively
50 researched. At the same time, the use of transition metal ion complexes for binding ions, with
51 subsequent changes in the photo-physical properties of the metal ion complex, has also been a
52 fruitful area of research.[8] More recently, the use of lanthanide ion complexes in anion
53 sensing has also become a fast growing area of research, where the anion sensing occurs via a
54
55
56
57
58
59
60

1
2
3 direct coordination at the metal ion itself.[9-13] In contrast to these developments, then he use
4
5 of a combination of two modes of binding, e.g. hydrogen bonding donors and metal ion
6
7 complexes, for anion recognition and sensing has been much less explored, and mostly
8
9 through the use of transition metal ions.[14] With the aim of developing such sensors for
10
11 anions using lanthanide ions, we have recently synthesised Tb(III) based cyclen complexes
12
13 that possess a di-aryl based urea pendant arm.[15] Here the hydrogen donating urea moiety
14
15 acted as an anion receptor, as well as a sensitizer, or an antenna, for the population of the
16
17 Tb(III) excited state. In this work, we showed, that the Tb(III) could be sensitized by
18
19 excitation of the antenna, and that the sensitization process could be modulated upon
20
21 recognition of several anions such as acetates and phosphates at the urea moiety in non-
22
23 aqueous solution. We also demonstrated that for this same system, at high concentration,
24
25 additional anion binding occurred at the lanthanide ion centre directly through the mechanism
26
27 of displacement of metal bound water molecules [16].
28
29
30
31
32

33
34 In this communication, we set out to further explore the use of a combination of
35
36 hydrogen bonding receptors and the lanthanides for anion sensing, by using acyclic ligands.
37
38 Here we describe the synthesis and the photophysical evaluation of **1₃Eu**, formed from the
39
40 *phen* based urea heteroditopic receptors **1** and Eu(III), and we demonstrate that the
41
42 photophysical properties of **1₃Eu** are significantly modulated upon recognition of anions in
43
44 organic solvent. While similar ideas have been developed by several other researchers such as
45
46 Hamilton *et al.*[17], Fabbrizzi *et al.*[18] Branda *et al.*[19] and Steed *et al.*[20], these examples
47
48 have all been based on the use of transition metal ions, and not lanthanide ions. Hence, the
49
50 formation of lanthanide complexes, has not, to the best of our knowledge, been achieved to
51
52 date.
53
54
55
56
57
58
59
60

RESULTS AND DISCUSSION

Synthesis: The synthesis of **1** was achieved in two steps from the commercially available 5-nitro-1,10-phenanthroline by firstly converting it to the corresponding amine **2** in 92% yield, by using hydrazine monohydrate in the presence of 10% Pd/C catalyst in ethanol at 95°C, followed by reaction with trifluoro-*p*-tolyl isocyanate, in chloroform at room temperature,



Scheme 1. Synthesis of **1** and the Eu(III) complex of **1**, **1₃Eu** (several structural isomers were expected to be formed).

which gave **1** as an off white precipitate, in 88% yield after recrystallization from a mixture of CHCl₃:MeOH,[21] Scheme 1. The synthesis of the Eu(III) complex of **1**, was accomplished by reacting **1** with 0.5 equivalents of Eu(CF₃SO₃)₃ in CH₃CN at room temperature overnight. The observed off white precipitate was isolated by filtration, and dried under vacuum to produce a bright yellow solid in a modest 28% yield. The successful synthesis of **1₃Eu** was supported by NMR spectroscopy and HRMS. Although the ¹H NMR was not greatly shifted (due to the presence of the paramagnetic Eu(III) ion), the formation of **1₃Eu** complex was clear in the ¹H NMR, which showed significant broadening for the *phen* protons, indicating the presence of a single species in solution possessing high symmetry. The ¹⁹F spectrum also revealed the presence of the CF₃ group at -60.56 ppm as well as a resonance at -78.29 ppm which we assigned to the triflate counter ions. The ESMS also showed the expected europium

isotopic distribution pattern for ${}^1_3\text{Eu}$, for instance for the m/z centred at 647 assigned to the $[\text{M}/2]$ peak.

Photophysical studies: The formation and the stability of the complex between Eu(III) and **1**, was investigated by observing the changes in the ground and the singlet excited state of **1** (10 μM), and the Eu(III) emission upon titration with $\text{Eu}(\text{CF}_3\text{SO}_3)_3$ in CH_3CN under ambient conditions. The changes observed in the absorption spectra of **1**, which had a λ_{max} of 265 nm and a shoulder at 320 nm, are shown in Figure 1.

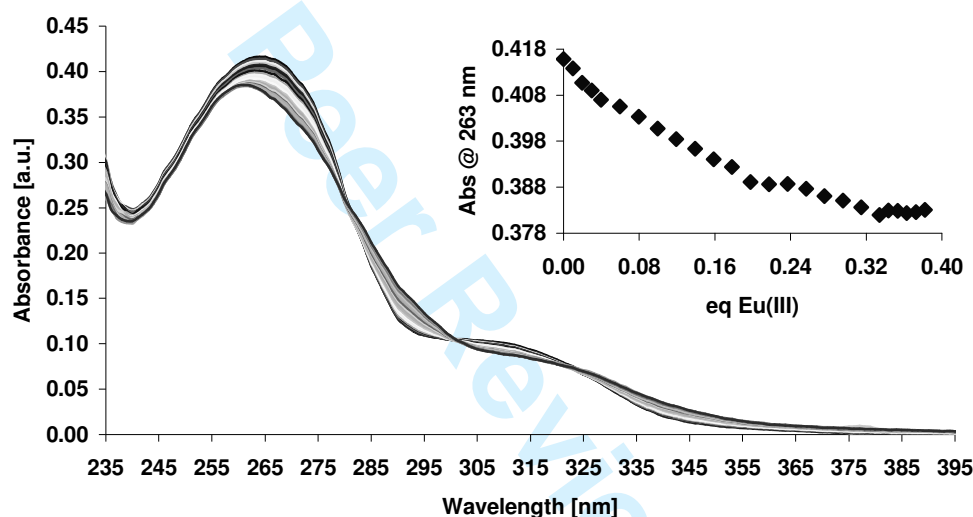


Figure 1. Changes on the absorption spectra of **1** (10 μM) upon addition of $\text{Eu}(\text{CF}_3\text{SO}_3)_3$.
Insert: The changes in absorbance at 263 nm as a function of equivalents of Eu(III).

Upon binding to Eu(III), small shifts were observed in the absorption spectra, where the 265 nm band was blue shifted to 260 nm, and the 320 nm shoulder was concomitantly red shift by ca. 5 nm. Three distinct isosbestic points were also observed at 280 nm, 300 nm, and 323 nm, respectively. The titration profile for the changes at 253 nm is also shown as an insert in Figure 1, which demonstrated the formation of a complex with 1:3 stoichiometry (e.g. ${}^1_3\text{Eu}$) as no significant changes occurred after ca. 0.33 eq. of Eu(III) added. The homogenous changes in the absorption spectra also demonstrate that the complex does not aggregate in solution.

The changes in the fluorescence emission were also monitored upon excitation at 265 nm and 320 nm. On both occasions, a broad band centred at 422 nm was observed. Upon addition of Eu(III), the emission intensity arising from this transition was quenched by 33%, without any changes in λ_{max} . By plotting the changes in the emission intensity at 422 nm versus equivalents of Eu(III), in a similar manner to that described above, again demonstrates the formation of the desired 1:3 stoichiometry in solution.

The formation of this complex was also clearly evident from the changes in the Eu(III) emission, Figure 2, which shows the formation of new bands centred at 594, 616, 652, and 700 nm, corresponding to the deactivation of the Eu(III) 5D_0 excited state to the 7F_J ground states ($^5D_0 \rightarrow ^7F_J$, $J = 1-4$), respectively. These results confirm that the *phen* ligand is capable

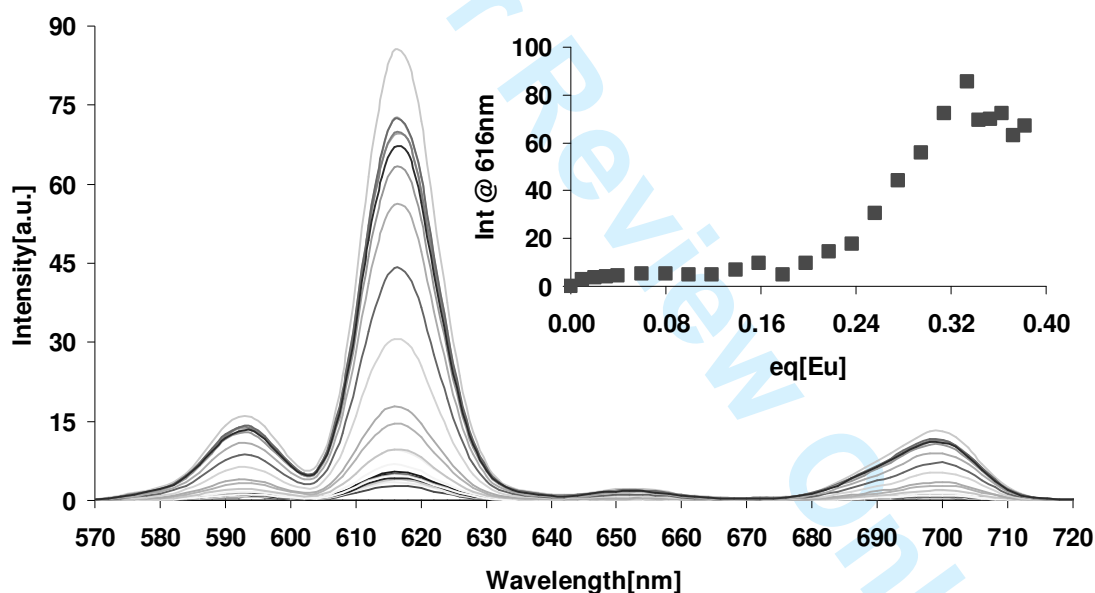


Figure 2. Changes on the Eu(III) emission of **1** (10 μM), which is enhanced upon addition of $\text{Eu}(\text{CF}_3\text{SO}_3)_3$. *Insert:* The changes in lanthanide emission at 616 nm as a function of equivalents of Eu(III) added, upon excitation at 265 nm.

of successfully sensitize the Eu(III) excited state. Furthermore, as can be seen in Figure 2, the $J = 2$ band, occurring at 616 nm, gave rise to large changes in the Eu(III) emission upon formation of 1_3Eu . This transition is highly sensitive to its coordination environment, so these results are indicative of direct coordination between the *phen* ligand and the Eu(III) ion.

Analysis of the changes in the $J = 2$, shown as inset in Figure 2, demonstrate the formation of the desired 1:3 complex, and its formation was further confirmed by using Job's plot analysis ($m/n = f_{\max} / (1 - f_{\max})$), gave $f_{\max} = 0.25$, and $m/n = 1/3$, for the changes in the 616 nm band.

The luminescence changes observed in Figure 2, were also analysed by fitting the data using the nonlinear least-squares fitting program SPECFIT. The results of this fitting are shown in Table 1, and demonstrate the stepwise formation of **1Eu**, **1₂Eu**, and **1₃Eu** complexes in solution, and that the **1₃Eu** complex is formed with $\log K_{1:3}$ of ~ 6 . Similar analysis was carried out on the changes observed in both the ground and the singlet excited state spectrum. On all occasions, the stepwise formation of **1₃Eu** was also observed, Table 1 (expressed as $\log \beta$) where a good correlation was observed between all three spectroscopic techniques.

Table 1. Binding constants and binding modes between Eu(III) and **1**, obtained upon fitting the changes in the absorption, the fluorescence and the Eu(III) emission.

Technique	Species (Eu _n :1 _m)	Log β	Std. Deviation
<i>Absorbance</i>	Eu1	3.86	0.012
	Eu1₂	7.54	0.016
	Eu1₃	13.46	0.031
<i>Fluorescence</i>	Eu1	3.88	0.008
	Eu1₂	7.48	0.016
	Eu1₃	13.38	0.024
<i>Phosphorescence</i>	Eu1	3.61	0.011
	Eu1₂	7.28	0.016
	Eu1₃	13.30	0.017

From Table 1, it is clear that the 1:3 stoichiometry dominates in solution, and hence the Eu(III) ion would be expected to be hexa-coordinated. The overall coordination number of **1₃Eu** was further confirmed, by measuring the hydration state (q), or the number of metal bound water molecules associated with the **1₃Eu** structure, by measuring the excited state lifetimes for the Eu(III) emission in H₂O and D₂O, respectively, by direct excitation of the Eu(III) centre at 395 nm. This gave values of 0.333ms and 1.83 ms for $\tau_{\text{H}_2\text{O}}$ and $\tau_{\text{D}_2\text{O}}$, respectively, which translates, using the Horrocks's modified equation [22] developed by

Parker *et al.*,[23], in to a q value of 2.6, confirming the overall coordination number of $\mathbf{1}_3\mathbf{Eu}$ as nine in aqueous solution.

Anion Sensing: Having successfully synthesised and, analysed the formation of $\mathbf{1}_3\mathbf{Eu}$ in solution, we next investigated its ability to bind/recognize anions. As $\mathbf{1}_3\mathbf{Eu}$ has three urea based ligands, all of which are capable of participating in the recognition of anions through hydrogen bonding, we expected to see significant changes in the photophysical properties of the complex upon such binding. Moreover, and as demonstrated above, the complex has three metal bound solvent molecules, all of which could be displaced by other competitive coordinating ligands, such as anions, with concomitant changes in the coordination environment of the lanthanide ion and hence, in its photophysical properties. Hence, the anion sensing ability of $\mathbf{1}_3\mathbf{Eu}$ could occur through either of these modes, or through the combination of both.

All of the three spectroscopic techniques discussed above were used to monitor the recognition of anions by $\mathbf{1}_3\mathbf{Eu}$ such as acetate, dihydrogenphosphate, fluoride and chloride as their tetrabutylammonium salts (TBA^+), in CH_3CN . Upon titrating AcO^- , the absorption spectrum was significantly affected as demonstrated in Figure 3. These changes were

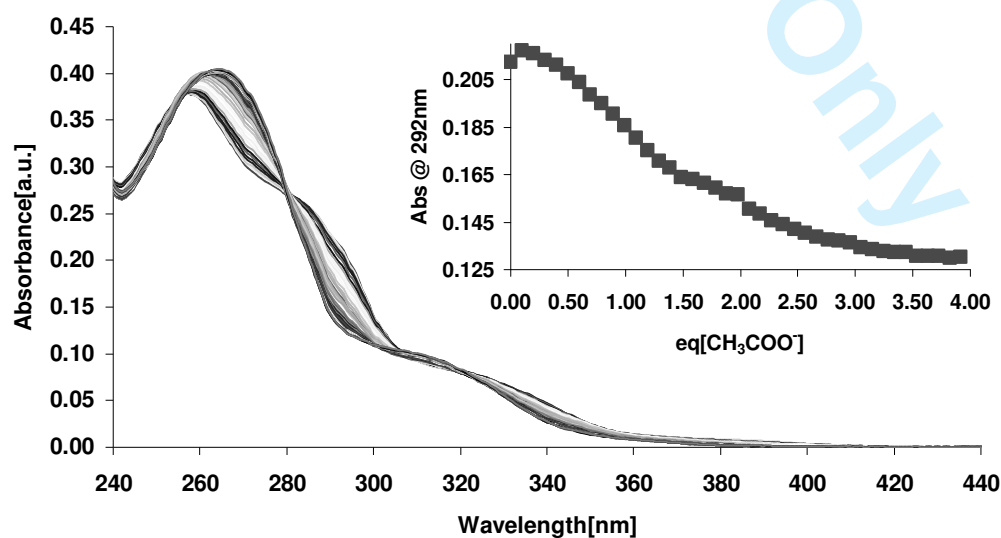


Figure 3. Changes on the absorbance of $\mathbf{1}_3\mathbf{Eu}$ (4 μM) upon addition of AcO^- . *Insert:* shows changes in absorbance at 292 nm as a function of equivalents of acetate added.

1
2
3 accompanied by the formation of four isosbestic points at 256, 280, 303 and 322 nm, which
4
5 were attributed to the interaction of the anion with the three urea moieties. Analysis of the
6
7 changes in the absorption spectrum is shown as an inset in Figure 3, and demonstrated that
8
9 these changes occurred up to ca. three equivalents of AcO^- , signifying the formation of
10
11 hydrogen bonding complexes between these anion and the urea moieties. Fitting this data
12
13 using SPECFIT, however, only gave accurate binding constants for two of these binding
14
15 events, namely the 1:1 and the 2:1 (ion:complex) between $\mathbf{1}_3\text{Eu}$ and AcO^- , with binding
16
17 constants $\text{Log } K_{1:1}$ and $\text{Log } K_{2:1}$ of 6.23 (± 0.257) and 6.17 (± 0.169), respectively for these
18
19 interactions. Similar changes were also observed in the absorption spectrum of $\mathbf{1}_3\text{Eu}$ for the
20
21 titration of H_2PO_4^- and F^- . As in the case of AcO^- , then for F^- we were only able to fit the
22
23 spectral changes of two binding events. However, for H_2PO_4^- , the best fits were observed only
24
25 when the data was fitted to binding events which involved the 1:1 and 1:2, complex formation
26
27 as well as the 2:1 and 2:2 complex between $\mathbf{1}_3\text{Eu}$ and H_2PO_4^- . In contrast to these results, the
28
29 titration of Cl^- , Br^- and I^- , gave only rise to the formation of 1:1 complexes. In the case of Cl^-
30
31 and Br^- , the changes in the absorption spectra of $\mathbf{1}_3\text{Eu}$ were of similar nature, at the same time
32
33 as being overall smaller to that observed above. However, in the case of I^- only absorption
34
35 enhancements were observed without the formation of clear isosbestic points.
36
37
38
39
40
41
42

43 The fluorescence emission of $\mathbf{1}_3\text{Eu}$ was also affected upon carrying out anion
44
45 titrations. After excitation at either 260 nm or 330 nm, fluorescence enhancements of 62%,
46
47 58%, 34%, 10%, and 16% were observed for AcO^- , F^- , Cl^- , Br^- , and I^- , respectively, with no
48
49 apparent shifts in the 420 nm band. These changes were analysed in the same manner as
50
51 described above for the ground state changes. As an example, then in the case of AcO^- ,
52
53 plotting the changes as a function of added equivalents, clearly showed that the changes occur
54
55 up to the binding of three equivalents of AcO^- , indicative of the 3:1 binding stoichiometry.
56
57
58
59
60 However, in the case of H_2PO_4^- , initial quenching was also observed of ca. 15%.

Nevertheless, after the addition of 0.5 equivalents of H_2PO_4^- , the emission was enhanced in a similar manner to that observed above.

However, from these spectroscopic anion titrations, the most significant changes were observed in the Eu(III) emission of **1₃Eu**, which was quenched up to *ca.* 2 equivalents of AcO^- (after initial slight enhancement $\sim 3\%$), Figure 4. The insert in Figure 4, also shows the

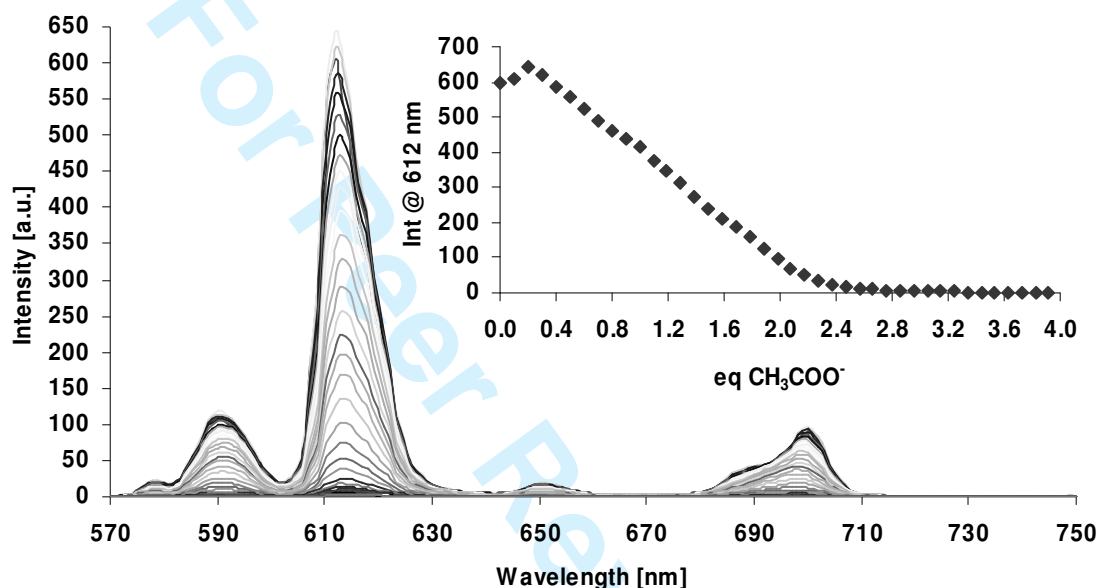
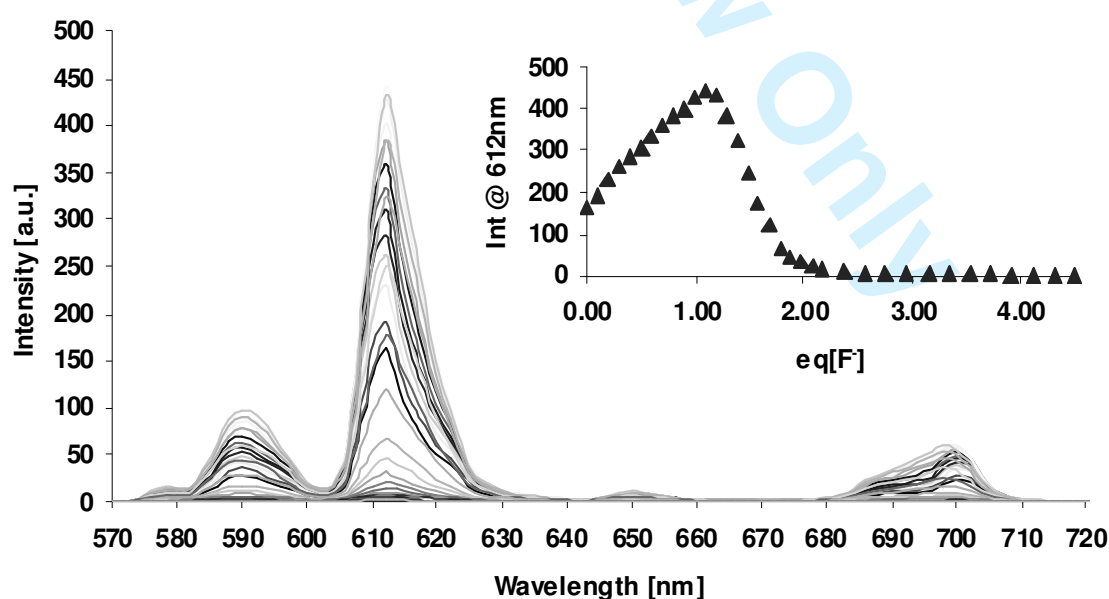


Figure 4. Changes on the lanthanide emission intensity of **1₃Eu** ($4 \mu\text{M}$), which was quenched upon titration with AcO^- . Insert shows changes in intensity at 612 nm as a function of added equivalents of AcO^- .

profile of the changes in luminescence intensity at 612 nm ($J = 2$ band) as a function of the number of equivalents of AcO^- added, and in a similar manner to that observed for the UV-Visible and fluorescence titrations above, demonstrates that two equivalents of AcO^- were needed to fully quench the lanthanide emission. We propose that this quenching can be attributed to an energy mismatch between the lowest triplet state (T_1) of the antenna and the excited state of europium, hence making the transfer of energy unfavourable from the triplet state of the antenna, T_1 , to the excited state of the Eu(III), $^5\text{D}_0$, upon anion recognition. Alternatively it is also possible that some contribution from dissociation, or displacement of **1** from the Eu(III) centre in **1₃Eu** could occur upon formation of hydrogen bonding complex

1
2
3 between the urea and the anions, however to date we have been unable to fully quantify if
4 such displacement is occurring. With the aim of evaluating these binding modes of the anion,
5 analysis of the changes seen in Figure 4 were undertaken using SPECFIT. As had been
6 observed for the changes in the ground state, the fitting of the changes observed in the AcO^- ,
7 showed that the 1:1 and the 2:1 stoichiometries were the most dominating, with $\text{Log } K_{1:1}$ and
8 $\text{Log } K_{2:1}$, of 6.56 (± 0.118) and 7.0 (± 0.061), which are in agreement with those values
9 observed from the ground and the singlet state changes. In a similar manner, H_2PO_4^- also gave
10 rise to luminescent quenching. However, these changes were best fitted using a variety of
11 binding equilibria such as 1:1, 1:2, 2:1 and 2:2, which would indicate that the anion bound
12 to ${}^3\text{Eu}$ in a more complicated manner than AcO^- . However, for both of these anions, the
13 main binding seems to be through hydrogen bonding at the urea moieties, with lesser
14 contribution from direct binding to the lanthanide centre, via the displacement of metal bound
15 solvent molecules.

16
17 However, such binding combination was observed for the titration of ${}^3\text{Eu}$ using F^- ,
18 Figure 5, where the Eu(III) emission was initially significantly enhanced up to ca. one



19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
Figure 5. The overall changes on the Eu(III) emission of $\text{Eu}:\mathbf{1}_3$ (4 μM) upon addition of F^- .
Insert: The changes in the intensity at 612 nm as a function of added equivalents of F^- .

1
2
3 equivalent of the ion, which we propose is due to the displacement of a metal bound solvent
4 molecule by F^- . However, these changes were subsequently followed by almost complete
5 quenching in the Eu(III) emission, as demonstrated in the insert in Figure 5 for the changes in
6 the 612 nm transition, in a similar manner to that observed for AcO^- above. This second
7 binding, we assign to the recognition of the anion at the urea site. From these luminescence
8 changes, analysis, using SPECFIT, gave good fitting of the experimental data, from which we
9 were able to obtain two binding constants, log K of 10.35 and 8.2 for the 1:1 and 1:2 bindings,
10 respectively. These are significantly higher binding values than observed for AcO^- or $H_2PO_4^-$,
11 respectively, which might further support the different mode of binding experienced by F^- . In
12 contrast to these results, the titration with Cl^- , Br^- and F^- , only gave rise to 1:1 binding, with
13 binding constant, $LogK_{1:1}$ of 6.34, 6.18, and 6.26, being determined for these anions,
14 respectively. From these results we have established, that only for F^- is the emission
15 enhanced, which demonstrates that the initial anion binding is caused by the binding of the
16 anion at the metal ion centre and that the second equivalent of the anion, binds to the complex
17 via hydrogen bonding interactions at the urea site, which gives rise to quenching in the Eu(III)
18 emission, as the efficiency of the sensitisation process is altered upon anion binding. Such
19 binding interactions were also observed for the other anions investigated herein. We are
20 currently in the process of evaluating these binding modes in greater detail as well as
21 developing analogue systems which possess higher Eu(III) binding affinities and
22 consequently could give rise to the sensing of anions by using such heteroditopic receptors
23 and lanthanide luminescence in a more competitive aqueous environment.
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54

55 CONCLUSION

56
57 In this communication, we have described the synthesis and the characterisation of a new
58 lanthanide complex between an urea based heteroditopic *phen* receptor and Eu(III). We
59
60

1
2
3 demonstrate, using ground, single excited and phosphorescence spectroscopy, that the
4
5 resulting complex is formed in 3:1 (ligand to metal ion) stoichiometry, and that this complex
6
7 can interact with anions in CH₃CN. In particular, in the case of AcO⁻, H₂PO₄⁻, Cl⁻, Br⁻, and
8
9 I⁻, the titration of these ions lead to significant changes in the Eu(III) emission, which was
10
11 fully quenched, in the case of AcO⁻, H₂PO₄⁻, within the addition of 3 equivalents of these
12
13 anions. This we propose as being the result of binding of these anions at the urea moieties in
14
15 **1₃Eu**. In contrast, the titration of F⁻, gave rise to initial enhancement in the Eu(III) emission
16
17 up to one equivalent, followed by luminescence quenching. This we assign to dual binding
18
19 modes involving initial binding of the anion at the metal ion centre itself, with concomitant
20
21 removal one solvent molecule, and enhancement in the Eu(III) emission, followed by
22
23 quenching in the Eu(III) emission upon binding of the anion at one or more of the urea
24
25 moieties in **1₃Eu**.
26
27
28
29
30
31
32
33

34 ACKNOWLEDGMENTS

35
36 We thank Trinity College Dublin, CSCB, SFI and IRCSET for financial support. We also like
37
38 to thank Dr. John E. O'Brien for his help.
39
40
41
42

43 EXPERIMENTAL

44
45 **General:** Reagents (obtained from Aldrich) and solvents were purified using standard
46
47 techniques. Melting points were determined using a Gallenkamp melting point apparatus.
48
49 Infrared spectra were recorded on a Mattson Genesis II FTIR spectrophotometer equipped
50
51 with a Gateway 2000 4DX2-66 workstation. ¹H NMR spectra were recorded at 400 MHz
52
53 using a Bruker Spectrospin DPX-400 instrument. ¹³C NMR spectra were recorded at 100
54
55 MHz using a Bruker Spectrospin DPX-400 instrument.
56
57
58
59
60

1
2
3 **1-[1,10]Phenanthroline-5-yl-3-(4-trifluoromethyl-phenyl)-urea (1):** To a suspension of the
4
5 amine (**3**) (1.0 g, 5.12 mmol) in CHCl₃ (40 mL) trifluoro-p-tolyl isocyanate (0.79 mL, 5.63
6
7 mmol) was added. After five minutes all the amine was dissolved, and a dark yellow solution
8
9 was observed. The reaction mixture was stirred overnight at room temperature, under an
10
11 argon atmosphere. An off white precipitate was observed on the reaction vessel. This
12
13 precipitate was filtered and washed with cold CHCl₃. The obtained solid was recrystallized
14
15 from MeOH to yield a pale solid (1.38 g, 88% yield). m.p. decomposes above 290°C;
16
17 Calculated for C₂₀H₁₄N₄OF₃ *m/z* = 383.1120 [M + H]. Found *m/z* = 383.1107. ¹H NMR (400
18
19 MHz, *d*₆-(CD₃)₂SO, δ_H): 9.55 (br s, 1H, NH), 9.16 (d, 1H, *phen*-CH, *J* = 4.0 Hz), 9.12 (br s,
20
21 1H, NH), 9.00 (d, 1H, *phen*-CH, *J* = 4.0 Hz), 8.65 (d, 1H, *phen*-CH, *J* = 8.5 Hz), 8.43 (d, 1H,
22
23 *phen*-CH, *J* = 8.0 Hz), 8.39 (s, 1H, *phen*-CH), 7.89 (dd, 1H, *phen*-CH, *J* = 4.0 Hz), 7.72 (m,
24
25 5H, *phen*-CH + Ar-CH); ¹³C NMR (100 MHz, *d*₆-(CD₃)₂SO, δ_C): 152.87, 149.87, 148.74,
26
27 145.89, 143.34, 143.13, 135.61, 132.08, 130.44, 128.50, 126.25, 126.22, 123.77, 123.68,
28
29 122.95, 122.21, 118.01, 116.07; ¹⁹F NMR (376 MHz, *d*₆-(CD₃)₂SO, δ_F): -60.58 (CF₃); MS
30
31 (ES⁺) *m/z* = 383.11 (M + H). IR ν_{max} (cm⁻¹) 3394, 3284, 3211, 3089, 1711, 1613, 1563, 1505,
32
33 1472, 1411, 1377, 1329, 1310, 1270, 1202, 1162, 1153, 1108, 1097, 1066, 1017, 988, 945,
34
35 878, 848, 826, 803, 737, 711, 691.

36
37 **Europium complex of 1, 1₃Eu:** To a suspension of the urea (**1**) (0.10 g, 0.26 mmol) in
38
39 CH₃CN (20 mL) was added Eu(CF₃SO₃)₃ (0.06 g, 0.11 mmol). Within few minutes a clear
40
41 yellow solution was observed. The reaction mixture was stirred overnight, at room
42
43 temperature under an argon atmosphere. The precipitate was isolated by filtration, and dried
44
45 under vacuum to produce a bright yellow solid in (0.13 g, 28% yield). ¹H NMR (600 MHz,
46
47 *d*₆-(CD₃)₂SO, δ_H): 9.52 (s, 1H, NH), 9.15 (br s, 1H, *phen*-CH), 9.10 (s, 1H, NH), 8.98 (br s,
48
49 1H, *phen*-CH), 8.64 (d, 1H, *phen*-CH, *J* = 8.6 Hz), 8.43 (d, 1H, *phen*-CH, *J* = 7.6 Hz), 8.35 (s,
50
51 1H, *phen*-CH), 7.88 (br s, 1H, *phen*-CH), 7.74 (d, 2H, Ar-CH, *J* = 8.6 Hz), 7.70 (br s, 1H,
52
53
54
55
56
57
58
59
60

1
2
3 *phen*-CH), 7.69 (d, 2H, Ar-CH, $J = 8.6$ Hz); ^{19}F NMR (376 MHz, d_6 -(CD_3) $_2\text{SO}$, δ_{F}): -60.56
4
5 (CF $_3$), -78.29 (CF $_3\text{SO}_3$); MS (ES $^+$) $m/z = 558.00$ [(M-2*phen* ligands) + Na] 648.95 [M/2],
6
7 684.91 [(M/2) + 2H $_2\text{O}$].; IR ν_{max} (cm $^{-1}$) 3334, 1656, 1605, 1542, 1412, 1314, 1223, 1160,
8
9 1107, 1066, 1026, 844, 808, 733, 719, 695.

References:

- 10
11
12
13
14
15
16 [1] Sessler, J. L.; Gale, P. A.; Cho, W. S., *Anion Receptor Chemistry*; Royal Society of
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
Chemistry: Cambridge, UK, 2006.
- [2] Gunnlaugsson, T.; Glynn, M.; Tocci (née Hussey), G. M.; Kruger, P. E.; Pfeffer, F. M.
Coord. Chem. Rev., **2006**, *250*, 3094; Gunnlaugsson, T.; Ali H.D.P.; Glynn, M.; Kruger, P.E.;
Hussey G. M. Pfeffer F. M.; dos Santos, C. M. G.; Tierney, J.; *J. of. Fluoresc.*, **2005**, *15*,
287. Gunnlaugsson, T.; Leonard J.P. *Chem. Commun.* **2005**, 3114; Leonard J.P.;
Gunnlaugsson T. *J. of. Fluoresc.* **2005**, *15*, 585.
- [3] Steed, J. W., *Chem. Commun.*, **2006**, 2637; Martínez-Mañez, R. Sancenón, F. *Chem. Rev.*,
2003, *103*, 4419. Suksai, C.; Tuntulani, T. *Chem. Soc. Rev.*, **2003**, *32*, 192 J. F. Callan, A.P.
de Silva, D.C. Magri, *Tetrahedron*, **2005**, *36*, 8551; deSilva, A.P.; Gunaratne, H.Q.N.;
Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher J. T.; Rice, T. E. *Chem. Rev.*
1997, *97*, 1515.
- [4] Gale, P. A., *Acc. Chem. Res.*, **2006**, *39*, 465. Gale P. A. *Chem. Commun.*, **2005**, 3761;
Gale, P.A. *Coord. Chem. Rev.*, **2001**, *213*, 79; Gale, P.A. *Coord. Chem. Rev.*, **2000**, *199*, 181.
- [5] Quinlan E.; Matthews S. E.; Gunnlaugsson, T., *Tetrahedron Lett.*, **2006**, *47*, 9333;
Palacios, M. A.; Nishiyabu, R.; Marquez, M.; Anzenbacher, Jr., P. *J. Am. Chem. Soc.*, **2007**,
129, 7538; Gómez D. E., Fabbrizzi, L., Licchelli, M., Monzani, E. *Org. Biomol. Chem.*, **2005**,
3, 1495; Pfeffer F. M.; Buschgens, A. M.; Barnett, N. W.; Gunnlaugsson, T.; Kruger, P. E.,
Tetrahedron Lett., **2005**, *46*, 6579; Pfeffer, F. M.; Gunnlaugsson, T.; Jensen, P.; Kruger, P.E.,

- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
- Org. Lett.* **2005**, 7, 5375; Gunnlaugsson, T.; Kruger, P. E.; Lee, T. C.; Parkesh, R.; Pfeffer, F. M.; Hussey, G. M.; *Tetrahedron Lett.*, **2003**, 44, 6575; Gunnlaugsson, T.; Davis, A.P.; Glynn, M. *Chem. Commun.*, **2001**, 2556.
- [6] Katayev, E. A.; Sessler, J. L.; Khrustalev, V. N.; Ustynyuk, Y. A. *J. Org. Chem.*, **2007**, 72, 7244; Evans, L. S.; Gale, P. A.; Light, M. E. Quesada, R. *Org. Biomol. Chem.*, **2006**, 4, 1019.
- [7] Pfeffer, F. M.; Lim K. F.; Sedgwick, K. J. *Org. Biomol. Chem.*, **2007**, 5, 1795; Bates, G. W.; Triyanti, Light, M. E.; Albrecht, M.; Gale, P. A. *J. Org. Chem.*, **2007**, 72, 8921.
- [8] Fabbrizzi, L.; Licchelli, M.; Rabaioli, G.; Taglietti, A. F. *Coord. Chem. Rev.* **2000**, 205, 85.
- [9] Leonard, J. P.; Nolan, C. B. Stomeo F.; Gunnlaugsson, T. *Top. Curr. Chem.*, **2007**, 281, 1; Gunnlaugsson T.; F. Stomeo, *Org. Biomol. Chem.*, **2007**, 5, 1999; Pope, S. J. A. *Polyhedron*, **2007**, 26, 4818; Pandya, S.; Yu, J.; Parker, D. *Dalton Trans.* **2006**, 2757; Shinoda, S.; Miyake, H.; Tsukube, H. *Handbook of the Physics and Chemistry of Rare Earths*; Elsevier North Holland, 2005; Vol. 35; Tsukube, H.; Shinoda, S.; *Chem. Rev.*, **2002**, 102, 2389; Parker, D. *Chem. Soc. Rev.*, **2004**, 33 156 Gunnlaugsson, T.; Harte, A. J.; Leonard, J. P.; Nieuwenhuyzen, M. *Chem. Commun.* **2002**, 2134.
- [10] Poole, R. A. Kielar, F.; Richardson, S. L.; Stenson, P. S.; Parker D. *Chem. Commun.*, **2006**, 4084; Parker, D. Dickins, R. S. Puschmann, H.; Cossland C.; Howard, J. A. K. *Chem. Rev.* **2002**, 102, 1977.
- [11] Plush, S.E; Gunnlaugsson, T. *Dalton Trans.*, **2008**, 3801.
- [13] S Plush, S.E; Gunnlaugsson, T. *Org. Lett.*, **2007**, 9, 1919.
- [14] Lankshear, M. D.; Cowley, A. R.; Beer, P. D. *Chem. Commun.* **2006**, 612; Tozawa, T.; Misawa, Y.; Tokita, S.; Kubo, Y. *Tetrahedron Lett.*, **2000**, 41, 5219; Kirkovits, G. J.; Shriver, J. A.; Gale, P. A.; Sessler, J. L. *Journal of Inclusion Phenomena and Macrocyclic Chemistry* **2001**, 41, 69-75; Reetz, M. T. In *Comprehensive Supramolecular Chemistry*; Atwood, L.,

1
2
3 Davies, J. E. D., MacNicol, D. D., Vogtle, F., Eds.; Pergamon: Oxford, 1996; Vol. 2, pp 553-
4 562; 7; Beer, P. D.; Timoshenko, V. Maestri, M.; Passaniti P.; Balzani, V. *Chem. Commun.*,
5 **1999**, 1755; Beer; P.D. *Chem. Commun.*, **1996**, 689.

6
7
8
9
10 [15] dos Santos, C. M. G.; Fernandez, P. B.; Plush, S. E.; Leonard, J. P.; Gunnlaugsson, T.
11
12 *Chem. Commun.*, **2007**, 3389.

13
14
15 [16] Gunnlaugsson, T.; Harte, A. J.; Leonard, J. P.; Nieuwenhuyzen, M. *Supramol. Chem.*
16
17 2003, 15, 505; Faulkner S.; Burton-Pye, B. P.; Khan, T.; Martin L. R.; Wray, S. D.; Sakabara,
18
19 P. J. *Chem. Commun.* **2002**, 1668; Dickins, R. S.; Gunnlaugsson, T.; Parker, D.; Peacock, R.
20
21 D. *Chem. Commun.* 1998, 1643.

22
23
24 [17] Goodman, M. S.; Weiss, J.; Hamilton, A. D. *Tetrahedron Lett.* **1994**, 35, 8943.

25
26 [18] Amendola, V.; Boiocchi, M.; Colasson, B.; Fabbrizzi, L. *Inorg. Chem.* **2006**, 45, 6138.

27
28 [19] Norsten, T. B.; Chichak, K.; Branda, N. R. *Chem. Commun.* **2001**, 1794.

29
30 [20] Turner, D. R.; Spencer, E. C.; Howard, J. A. K.; Tocher, D. A.; Steed, J. W. *Chem.*
31
32 *Commun.* **2004**, 1352; Turner, D. R.; Smith, B.; Spencer, E. C.; Goeta, A. E.; Evans, I. R.;
33
34 Tocher, D. A.; Howard, J. A.; Steed, J. W. *New J. Chem.* **2005**, 29, 90.

35
36 [21] dos Santos, C. M. G.; McCabe T.; Gunnlaugsson, T. *Tetrahedron Lett.*, **2007**, 48, 3135.

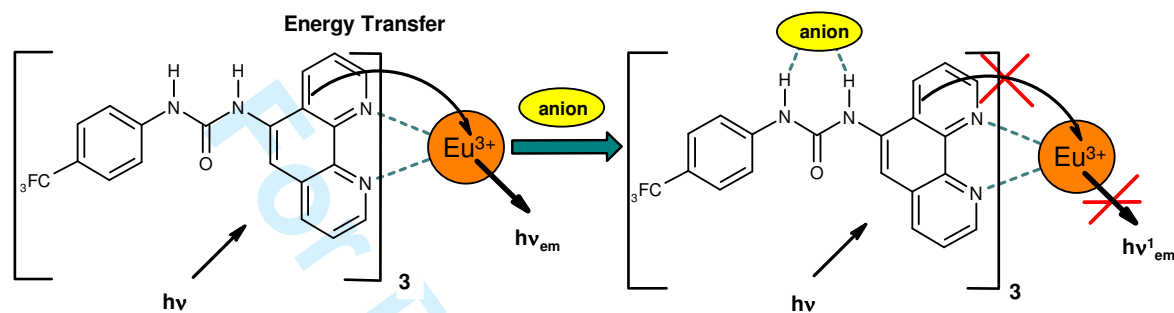
37
38 [22] Supkowski, R. M.; Horrocks, W. D. *Inorg. Chem. Acta.*, **2002**, 340, 44.

39
40 [23] Beeby, A.; Clarkson, I. M.; Dickens, R. S.; Faulkner, S.; Parker, D.; Royle, L.; de Sousa,
41
42 A.S.; Williams, J.A.G.; Woods, M. J. *Chem. Soc, Perkin Trans.*, 2, **1999**, 493.

Graphical abstract

Exploring the luminescent sensing of anions by the use of an urea functionalized 1,10-phenanthroline (phen) based (3:1) Eu(III) complex

Cidália M. G. dos Santos and Thorfinnur Gunnlaugsson



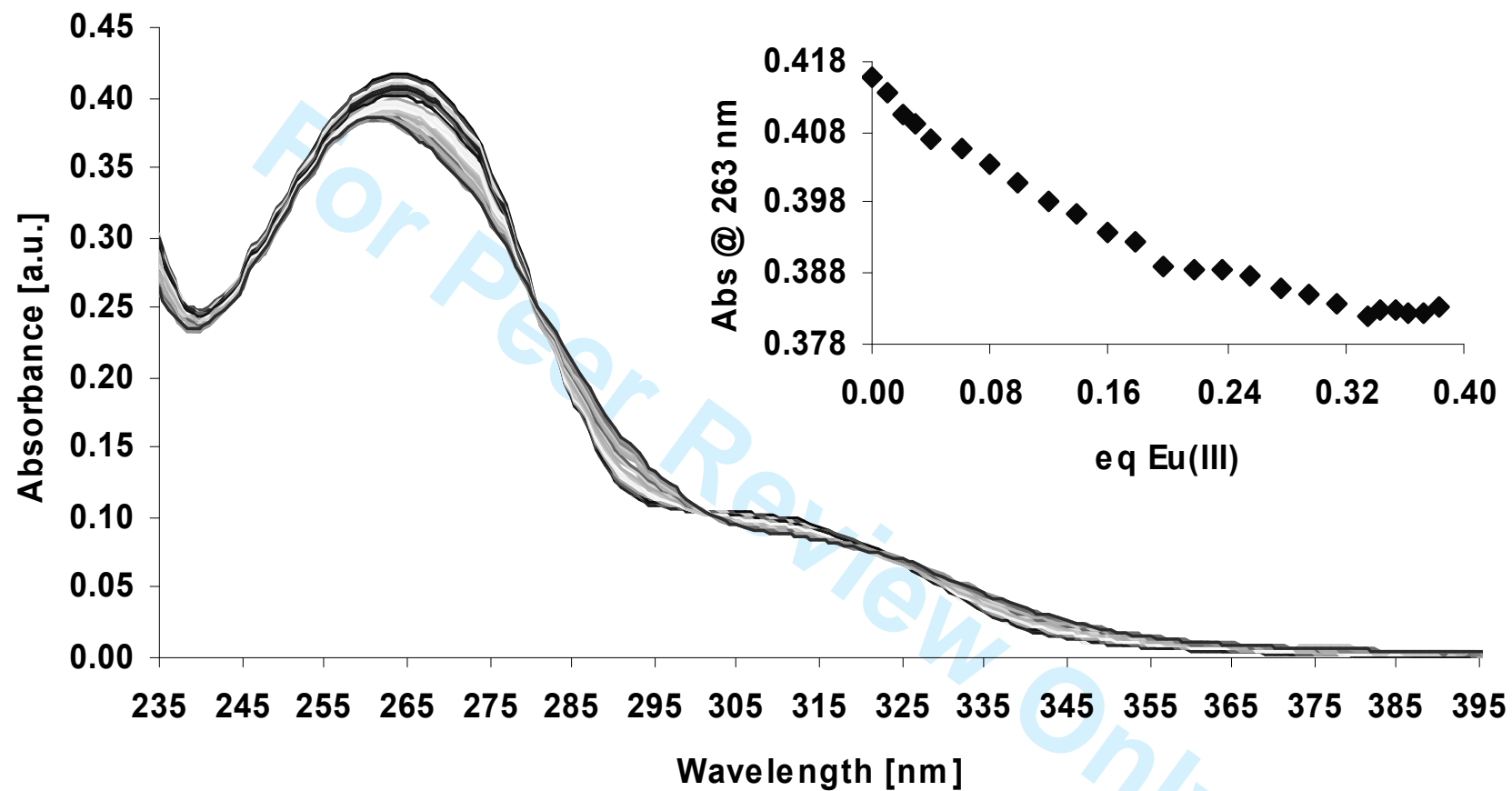


Figure 1

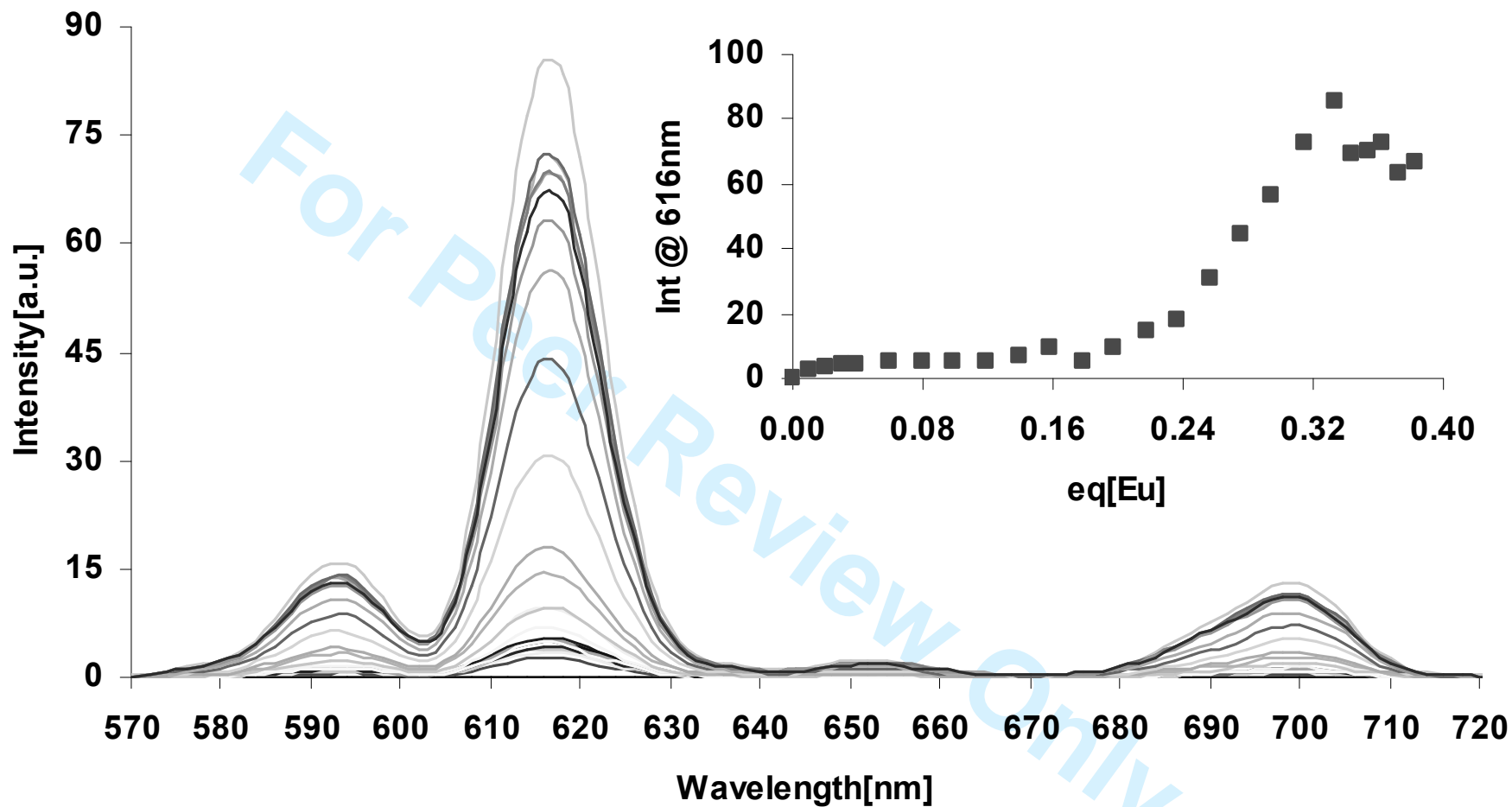


Figure 2

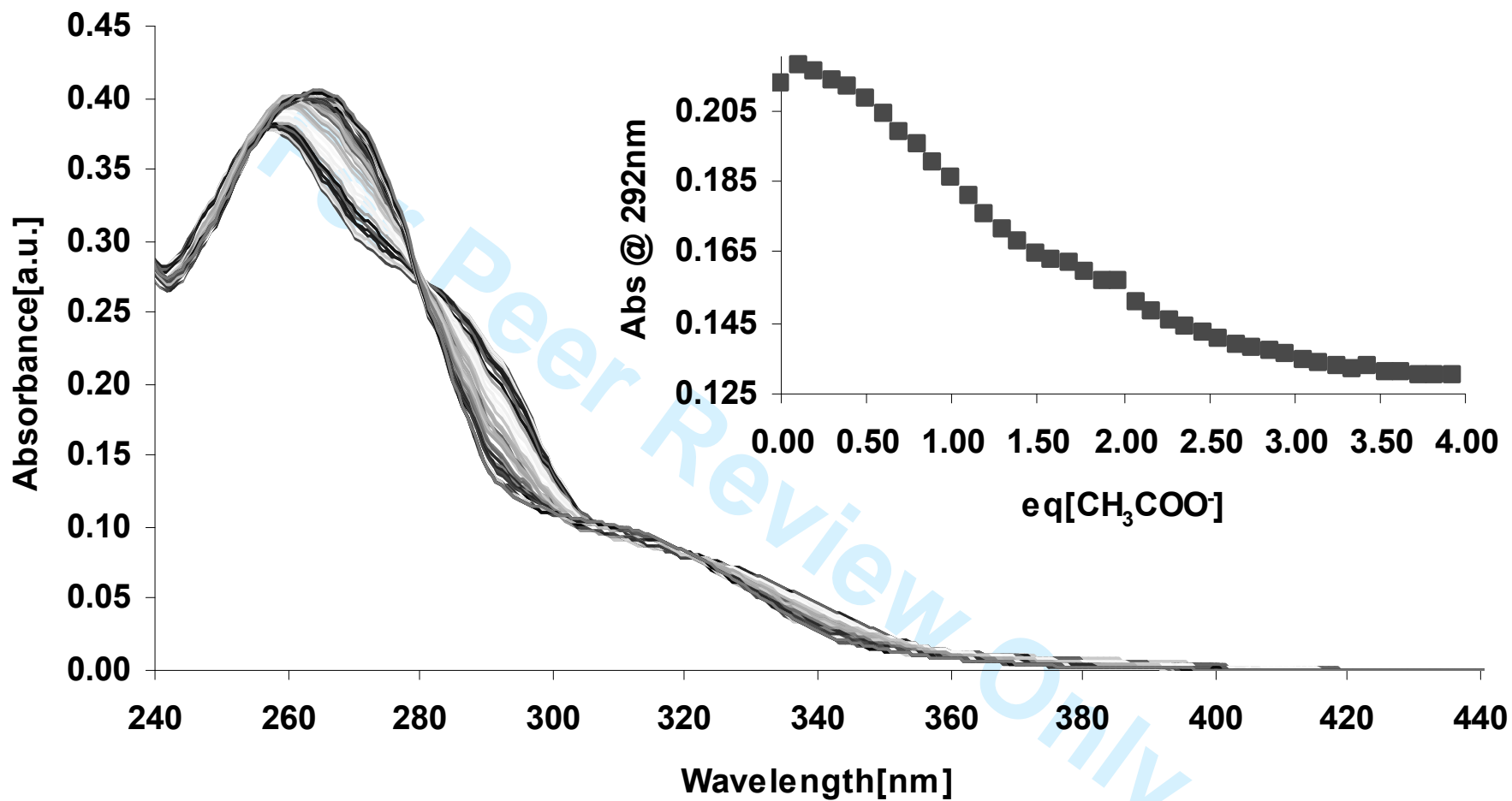


Figure 3

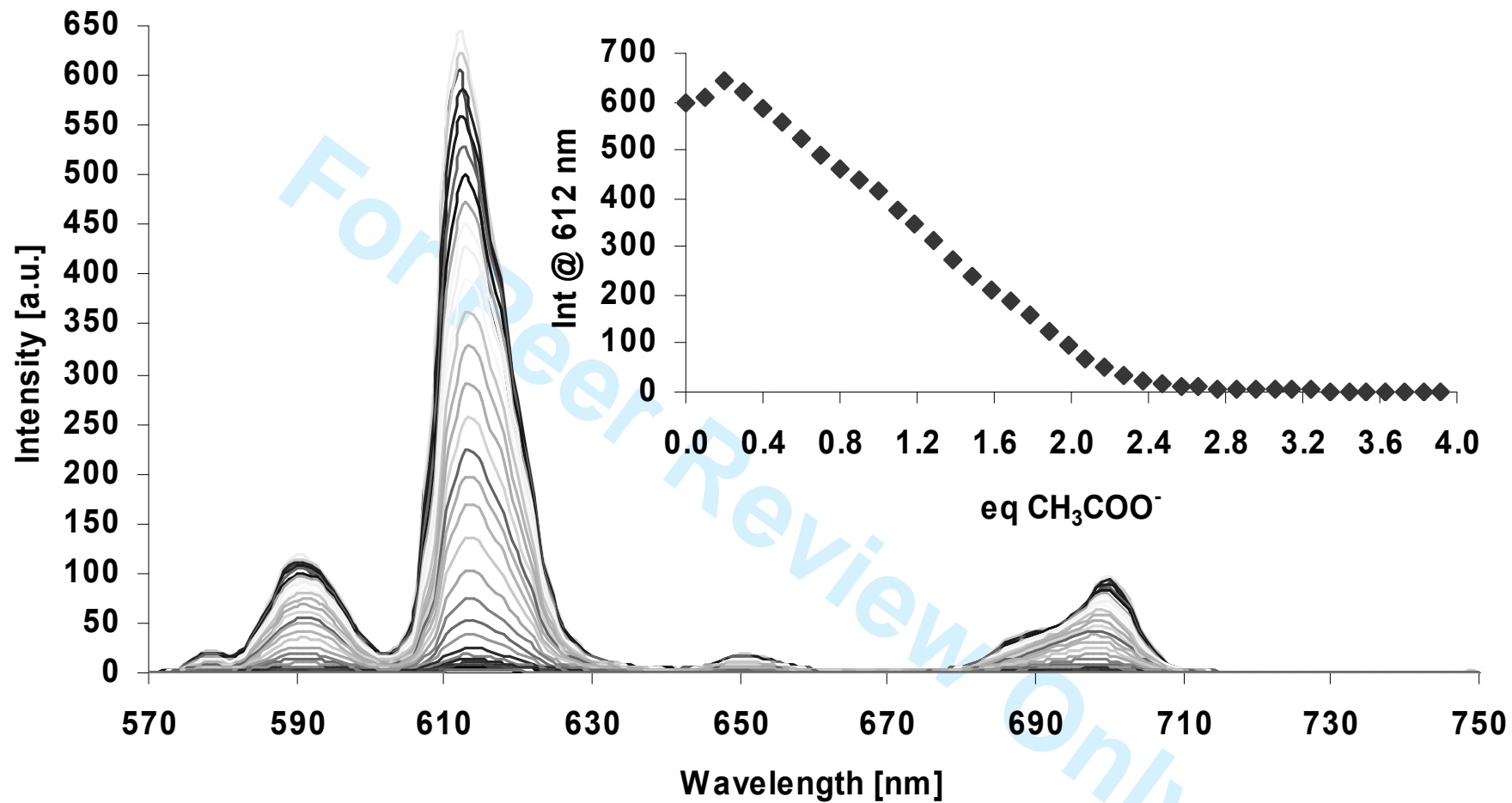


Figure 4

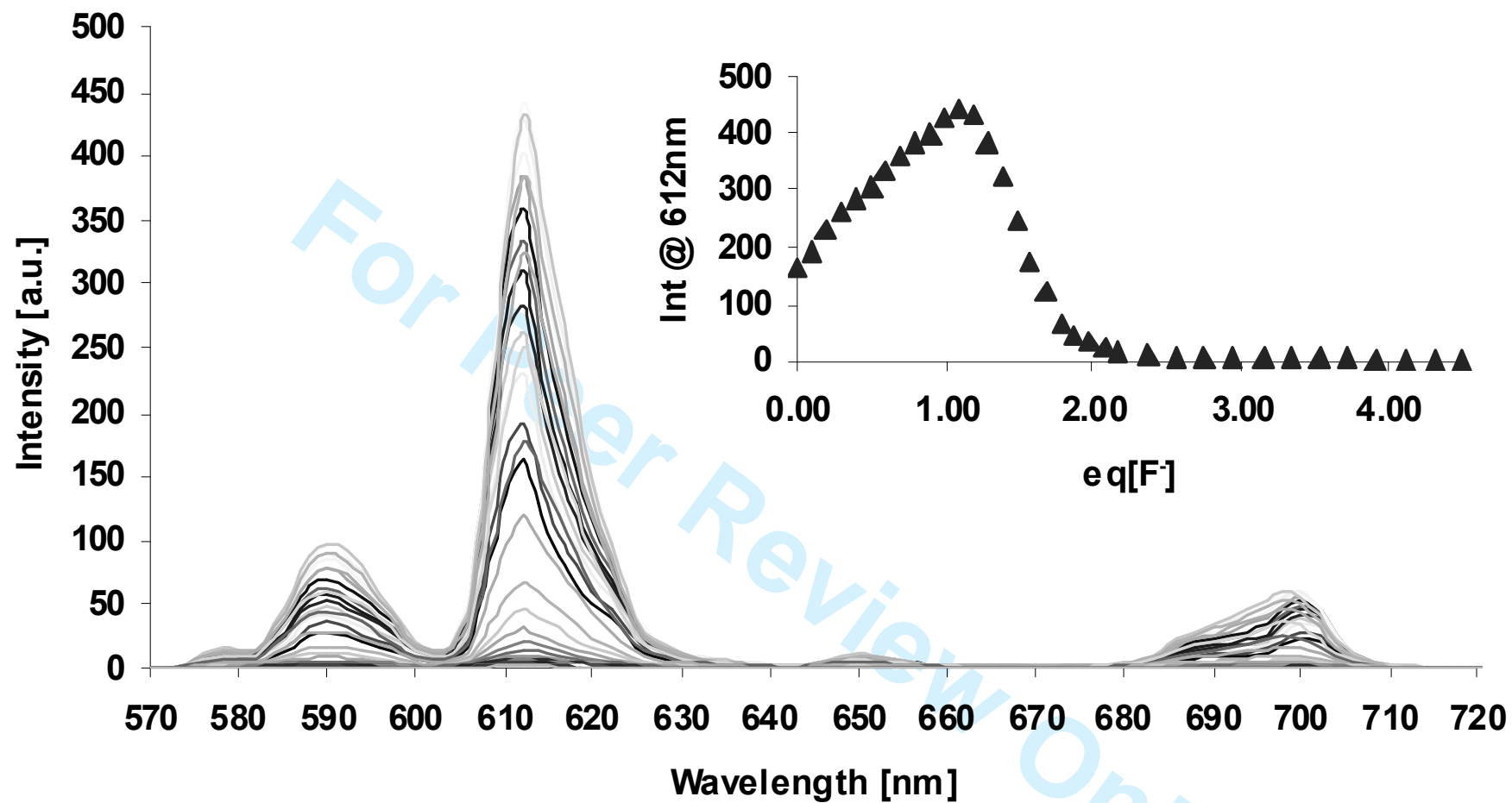


Figure 5

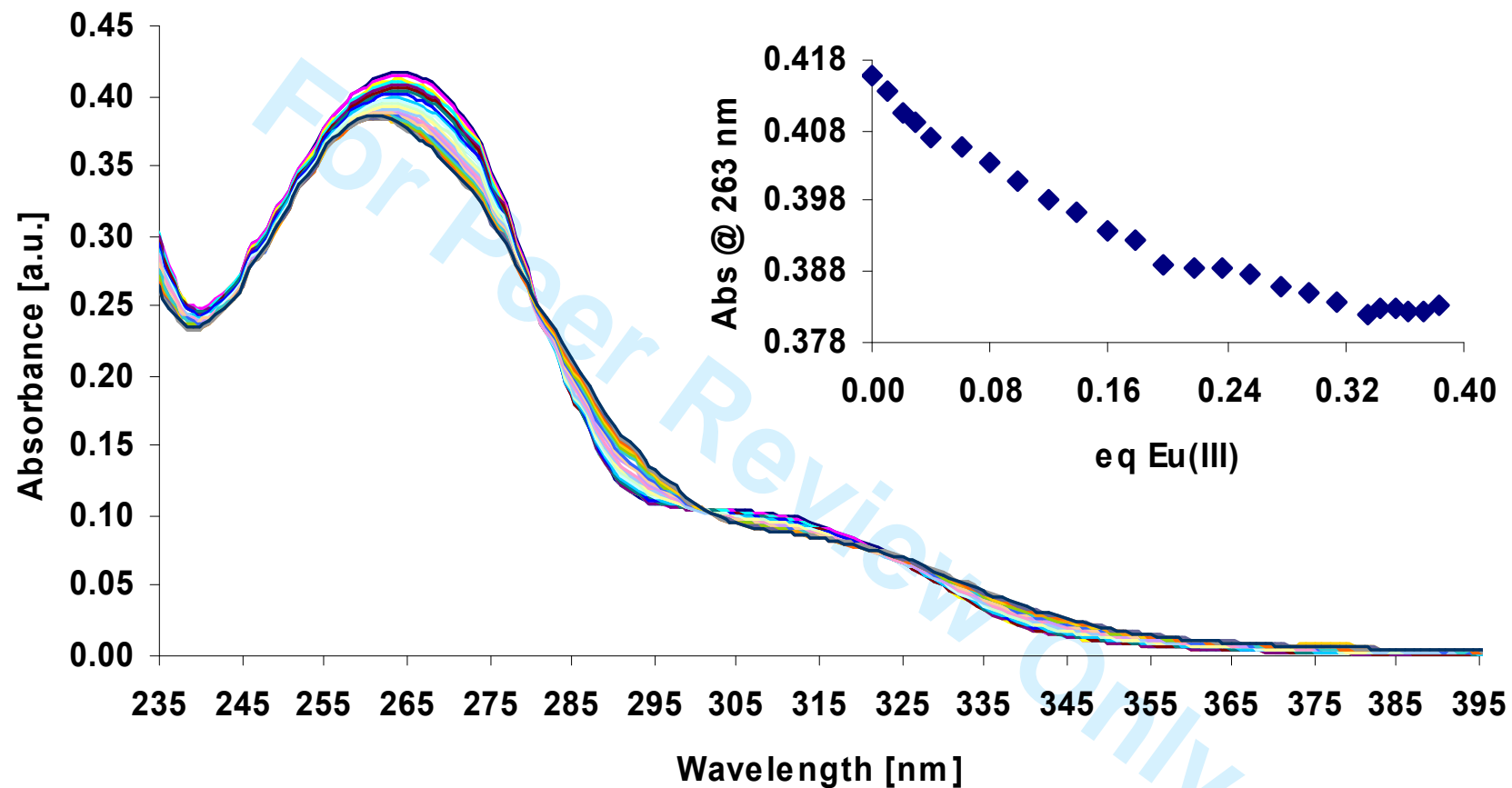


Figure 1

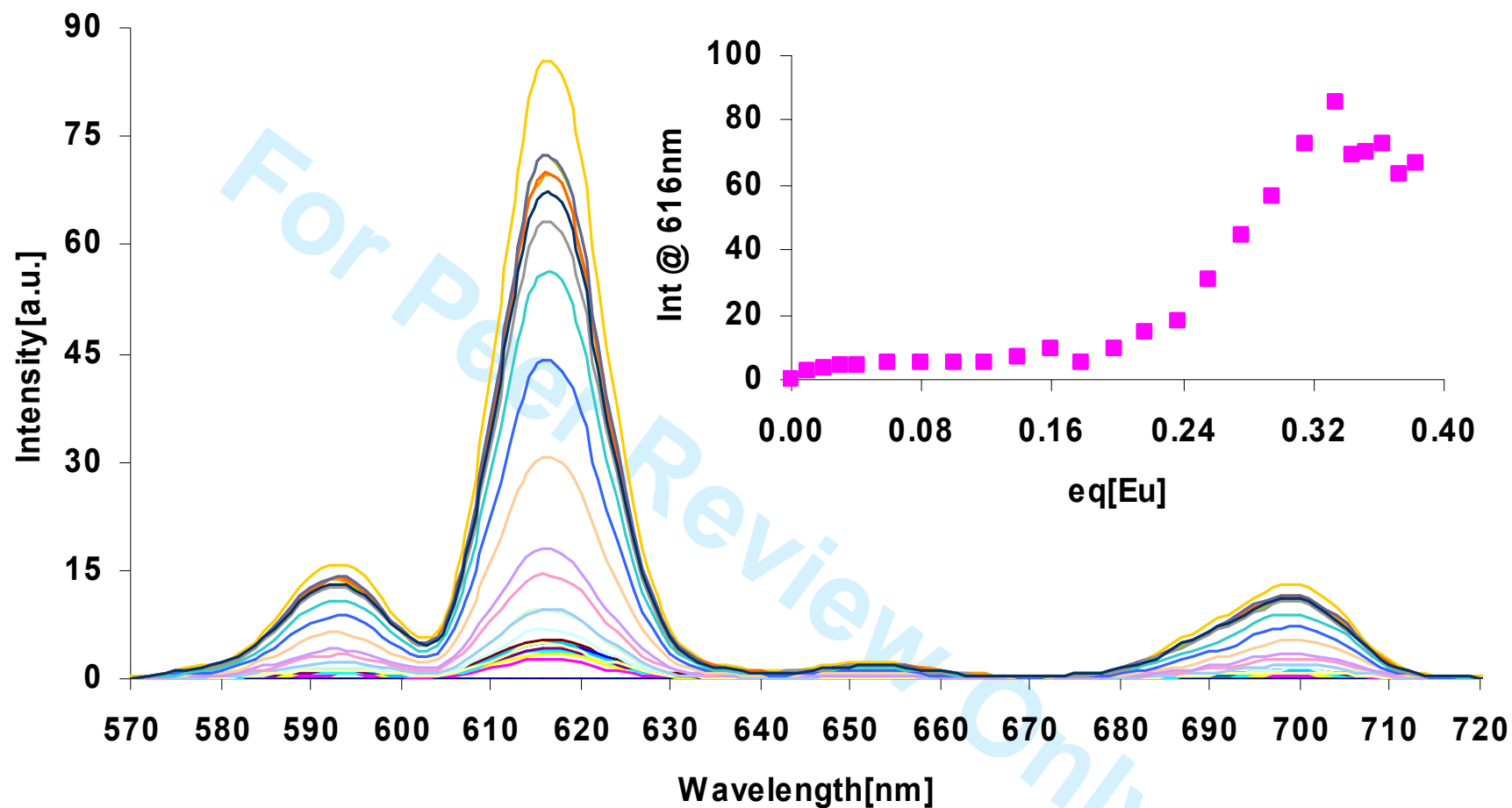


Figure 2

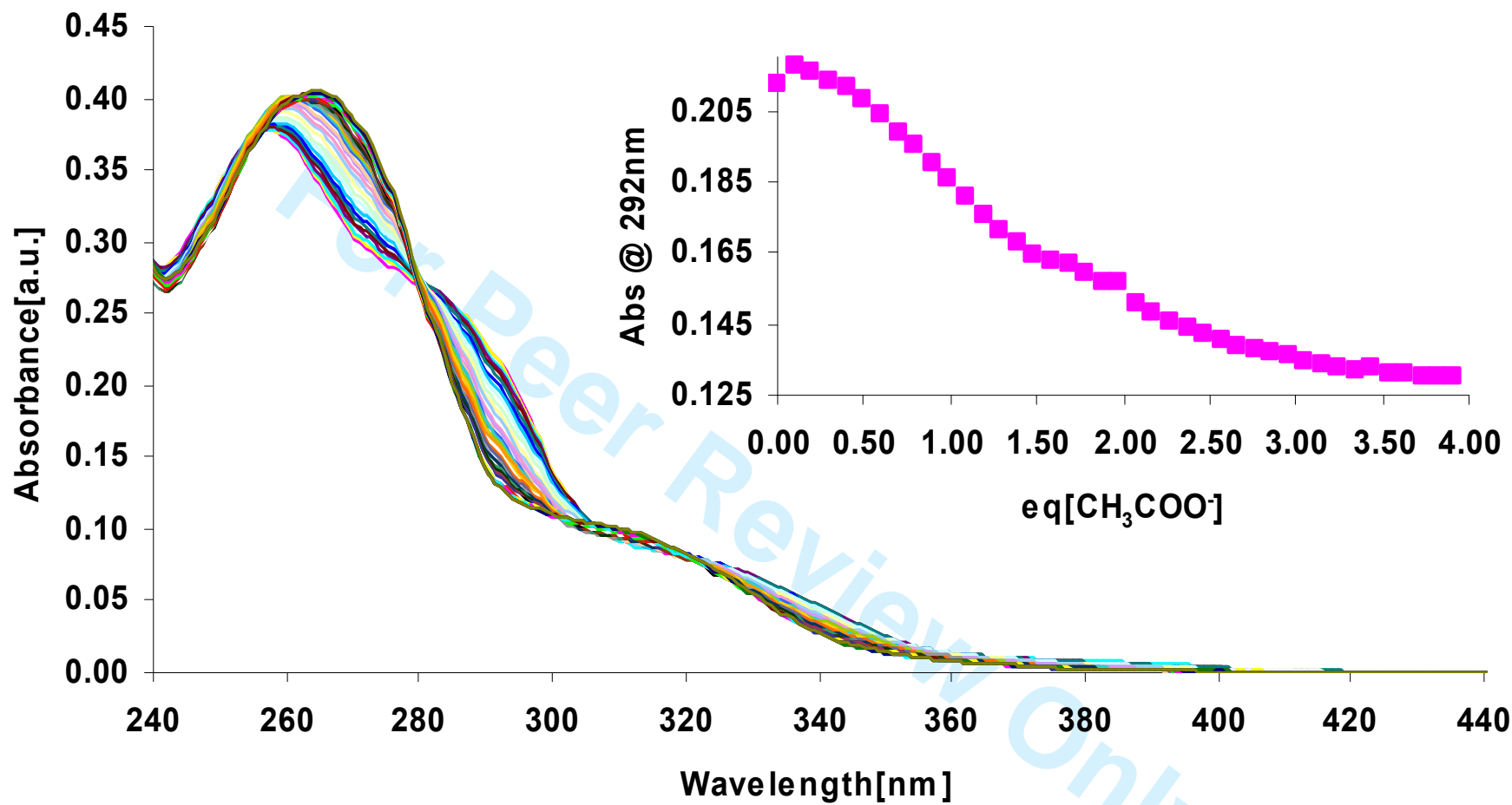


Figure 3

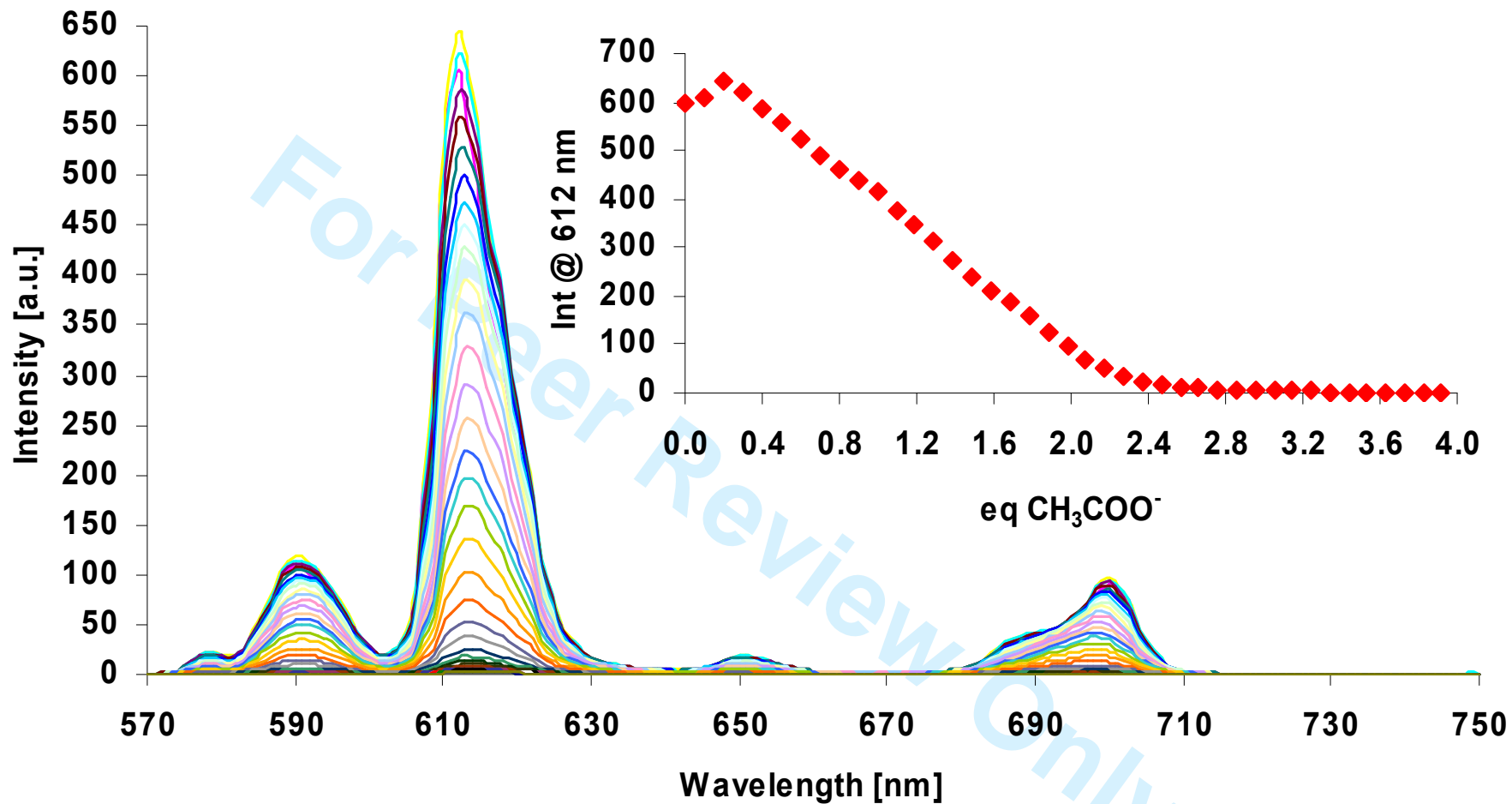


Figure 4

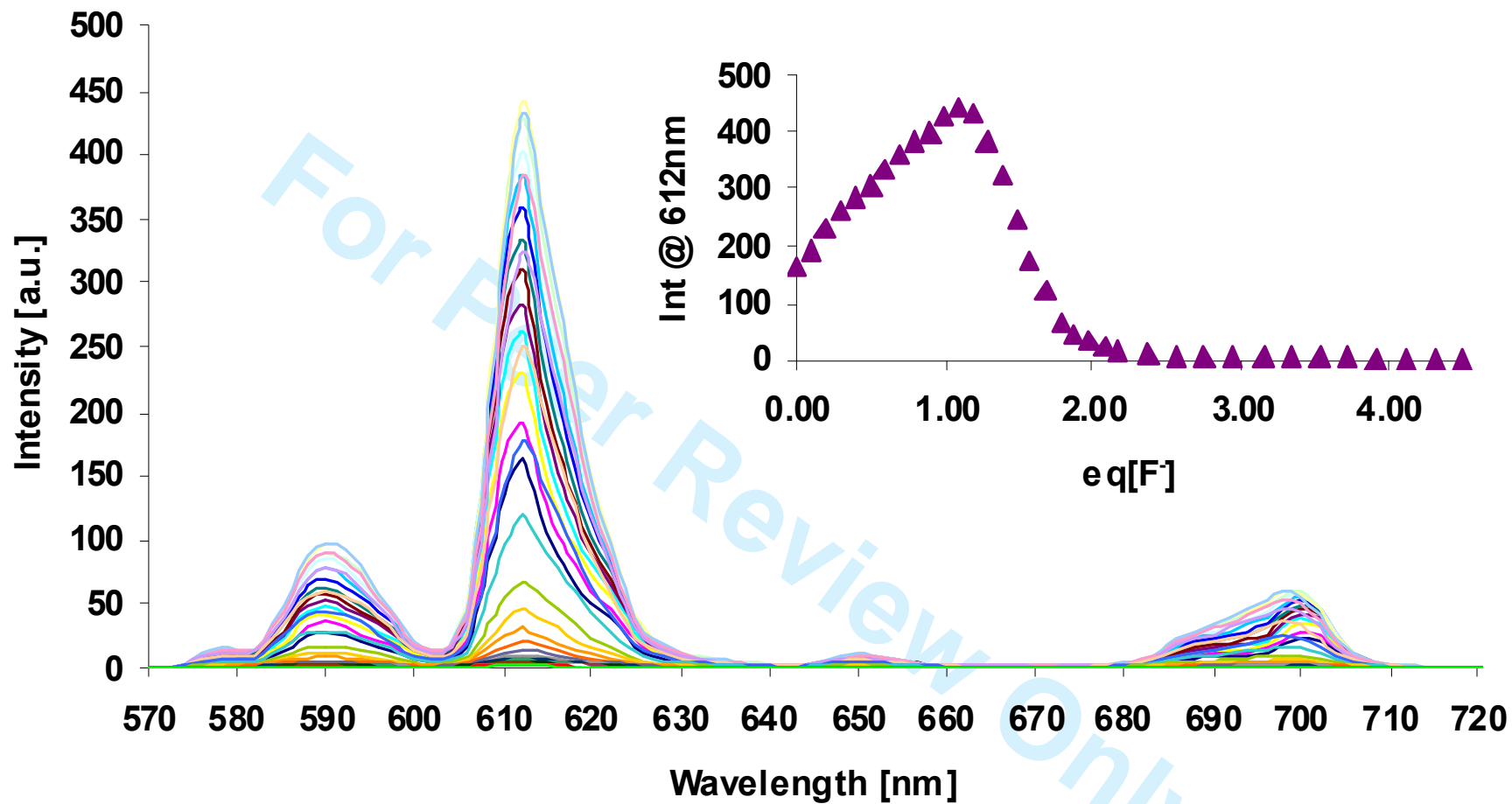


Figure 5