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Controllable three-component luminescence from a 1,8-naphthalimide/ Eu(III) complex: white light emission from a single molecule[†]

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A macrocycle-appended naphthalimide derivative and its Eu(III) complex show triple luminescence from isolated naphthalimide (blue), aggregated naphthalimide excimers (green) and Eu centres (red) with the balance being sensitive to the degree of aggregation, allowing white light emission to be obtained from a single molecule.

Emission of white light from a single molecule is an important chemical target as it will considerably simplify the preparation of luminescent display and lighting devices by removing the need for two or three separate components (e.g. red/blue/green luminophores) which may degrade at different rates or have different requirements for device fabrication.¹ In molecular species, white-light emission has been achieved in various ways. De Cola et al. used a combination of blue-emitting Ir and red-emitting Eu units to generate white light from a dinuclear Ir(III)/Eu(III) complex,² an approach which we have also investigated.³ Williams and co-workers took a different approach by using a combination of blue luminescence from mononuclear Pt(II) complexes and the red luminescence resulting from excimer formation when the complex aggregates in different solvents, thereby achieving a solvent-dependent balance of blue and red-emission bands from the same molecule.⁴ A balance between monomer and excimer or exciplex emission has also been used by other groups to generate white light emission,⁵ and a feature of this method is that it allows a degree of tunability by controlling the degree of association between monomer units and hence the balance between high- and low-energy emissive components.4,5 With a combination of blue and green emitting organic chromophores and a red-emitting Eu(III) unit, three-colour R/G/B emission from a single molecule has been achieved in some cases generating white light emission overall.⁶ A variety of other approaches has also been studied including preparation of a molecule containing complementary blue- and orange-emitting units between which energy-transfer is blocked because of the requirement for excitedstate proton transfer, leading to concentration-independent white luminescence;⁷ and a deceptively simple mononuclear Ir(III) complex which shows broad, panchromatic (white) luminescence from a mixed excited state has been reported.8

In this communication we report a new approach to this problem that uses a combination of solvent-dependent aggregation of a functionalised aromatic (1,8-naphthalimide) chromophore to generate tunable blue or blue/green luminescence, plus partial naphthalimide \rightarrow Eu(III) energy-transfer to generate some additional sensitised red luminescence. The result is highly aggregation-dependent luminescence that can be white in the correct solvent composition and also in the solid state.

1,8-Naphthalimide has several properties which make it ideal for use in this context. It shows short-lived (<1 ns) blue fluorescence from the singlet π - π * state, and efficient intersystem crossing to the lowest triplet state ($\phi_{\rm ISC} \approx 0.95$) which acts as energy-donor to Eu(III).⁹ The energy of this triplet state (18500 cm^{-1}) is just high enough to sensitise the emissive ${}^{5}\text{D}_{0}$ state of Eu(III) (17 500 cm⁻¹).¹⁰ In addition, aggregation of 1,8naphthalimide units can result in formation of excimers which fluoresce at lower energy than the monomer fluorescence: this is not normally seen in monomeric naphthalimides, but occurs in covalently-linked bis-naphthalimides in which the two fluorophores are held close together.¹¹ Thus energy-transfer from the naphthalimide triplet state to generate red emission from Eu(III) is possible, and - if aggregation can be induced the fluorescence from the singlet state can be varied with a balance of blue and green components.

The structural formula of the naphthalimide/macrocycle ligand H_3L is shown in Scheme 1. H_3L has a heptadentate binding domain which will give kinetically inert Ln(III) complexes,¹² and we prepared from this EuL and GdL, the latter to use in control experiments. Full details of all synthesis and characterisation, including electronic absorption spectra (Fig. S1), are in Supporting Information.

The effect of solvent-induced aggregation on luminescence is shown by the free ligand H_3L . In aqueous solution the fluorescence spectrum shows the typical intense band centred at 396 nm, extending down into the blue region of the visible spectrum. An isoabsorbing solution of H_3L in MeCN shows a



Scheme 1 Structural formulae of the compounds in this paper.

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Fig. 1 Luminescence spectra of H_3L in water (squares) and MeCN (circles) based on isoabsorbing solutions at the excitation wavelength. $\Phi = 0.022$ in 1:1 MeCN/water.

reduced intensity and slight changes in the relative intensities of the vibronic components for this fluorescence band and an additional broad low-energy feature centred at 475 nm which is characteristic of an excimer (Fig. 1).¹¹

Given the nature of H_3L it is possible that both π - π stacking between naphthalimide units, and hydrogen bonding involving H-bond donors (-CO₂H groups) and H-bond acceptors (the naphthalimide N and O atoms) on different molecules, contribute to the aggregation. The ¹H NMR spectrum of H_3L in MeCN is broad and poorly-defined, characteristic of aggregation, but the spectrum becomes sharp as soon as a few drops of water are added to the sample (Fig. S2). This implies that H-bonding plays an important role in aggregation of H_3L in solution, even though the excimer emission component must arise from π -stacking between the aromatic naphthalimide units.

The luminescence spectrum of EuL in water likewise is dominated by the naphthalimide fluorescence peak centred in this case at 385 nm. In addition we can see the series of line-like emission bands at lower energy that is characteristic of Eu(III) with the most intense component, as usual, being the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ line at 615 nm (Fig. 2, red line). This combination of intense blue/ violet and weaker red emission components generates overall purple emission with coordinates of 0.23, 0.10 in the standard CIE colour coordinate system. In contrast, in MeCN some aggregation occurs and we see (for an isoabsorbing solution



Fig. 2 Luminescence spectra of EuL in different solvents; all solutions were isoabsorbing at the excitation wavelength. Solvents were water/MeCN mixtures with the following water: MeCN proportions: red, 100:0; blue, 75:25; green, 50:50: cyan, 25:75; black, 0:100. The inset shows how the CIE coordinates vary: the coordinates based on the blue, green and cyan spectra overlap closely. The arrow shows the direction of change as the MeCN proportion increases; "X" denotes the pure white point (0.33, 0.33).

compared to the luminescence spectrum in water; Fig. 2, black trace, and Fig. 3) a reduction in intensity and change in shape (cf. Fig. 1) of the higher energy fluorescence band and the appearance of the lower-energy excimer emission component centred at about 460 nm which extends down into the green region of the spectrum. Given that hydrogen-bonding between molecules of EuL is not possible in the way that it is for H₃L due to the absence of acidic protons to act as donors, this aggregation to give excimer emission most likely arises from π -stacking. The balance between these two higher-energy emission components in MeCN is somewhat concentration-dependent, but at a concentration of 8 µM we see three emission components from a single molecule in the blue, green and red regions that combine to give light with CIE coordinates of 0.27, 0.25 (Fig. 3) which is at the blue end of the region generally considered "white" (CCT = 19500 K).‡

To investigate the kinetics of the naphthalimide \rightarrow Eu energy-transfer process we used transient absorption spectroscopy to examine its triplet state. Excitation of EuL at 355 nm in degassed MeCN resulted in appearance of an excited-state absorption spectrum whose main feature is at 470 nm, with weaker bands at 440 and 370 nm, exactly characteristic of the naphthalimide π - π * triplet excited state (Fig S3);^{9,10a} the decay of the transient absorption spectrum allowed determination of the lifetime of this triplet excited state to be 11 µs.

Time-resolved measurements on the 615 nm sensitised Eu-based emission band in MeCN revealed – in addition to the expected slow decay ($\tau = 1.1 \text{ ms}, \Phi = 0.128^{12}$) – a grow-in with a time constant of 14 µs (Fig. S4, ESI†). This matches well the 11 µs decay of the donor (naphthalimide triplet state), confirming the occurrence of naphthalimide \rightarrow Eu(m) energy-transfer in EuL. We also compared the Eu emission lifetime for EuL in H₂O and D₂O from which a hydration number of 2 was found for the Eu(m) centre, as expected given the 7-coordinate environment provided by the ligand.¹³

Given the different CIE colour coordinates of EuL in water and MeCN, we investigated the luminescence in mixed MeCN/water systems of different proportions but at a fixed concentration. We observed a smooth variation in luminescence colour from purple (in water) to white (in pure MeCN) as shown in Fig. 2, with the arrow in the inset showing the direction of change of the colour as the proportion of water in



Fig. 3 Expansion of the luminescence spectrum of EuL in MeCN (black trace in Fig. 2) showing clearly the three separate luminescence components (A, isolated naphthalimide; B, naphthalimide excimer; C, europium), with (inset) a picture of the luminescence from a sample of EuL under these conditions. * = Raman scattering artefact.



Fig. 4 Luminescence spectra of H_3L (green), EuL (red) and GdL (blue) as isoabsorbing thin films. The insets show (a) white emission from solid H_3L ; (b) bright cyan emission from EuL; and (c); how the CIE coordinates for the three compounds vary.

the solvent mixture decreases. Part of this is due to the known reduction in fluorescence quantum yield (blue component) as the solvent polarity is decreased,⁹ but as water disappears from the solvent mixture the lower-energy excimer feature starts to become significant as aggregation occurs and the blue/green balance changes. Thus the overall emission colour can be tuned according to solvent composition which alters the balance between the three emission components.

Finally, given the effect of aggregation on the luminescence of these compounds, we examined their luminescence in thin films (prepared by slow evaporation of MeOH solutions on a quartz plate). Fig. 4 shows luminescence spectra of H₃L, GdL and EuL measured using isoabsorbing thin films. Solid H₃L showed none of the UV/blue emission characteristic of isolated naphthalimide molecules: instead a broad emission band spanning the visible spectrum, but centred at 480 nm, was observed (Fig. 4) because of aggregation effects. Surprisingly, the colour of this broad luminescence of H₃L alone is in the white region (CIE coordinates 0.28, 0.35; CCT = 7800 K)‡; however it is relatively weak, probably because luminescence is quenched by electron-transfer from the tertiary amine of the macrocycle. Binding of Gd(III) into the macrocycle prevents this quenching and the emission of GdL is much stronger (Fig. 4) but it appears blue (CIE coordinates 0.19, 0.31; CCT = 21900 K)[‡], because the red tail of the emission spectrum of GdL is reduced compared to H₃L (see Fig. S5, ESI, for comparison of normalised spectral profiles), which must arise from differences in solid-state aggregation because GdL cannot hydrogen-bond to itself. In EuL however, addition of the sensitised Eu-based luminescence restores some of the red component that is missing from the luminescence of solid GdL, affording bright cyan luminescence from solid EuL (CIE coordinates 0.21, 0.31; CCT = 17600 K;‡ Fig. 4).

In conclusion, the combination of tunable emission in the blue/green region from the naphthalimide chromophore according to its degree of aggregation, and a sensitised red emission component from a Eu(III) centre in the same molecule, allows tunable three-component emission from a single molecule which appears white under some conditions. In solution EuL shows white emission in MeCN solution from a balance of purple/blue (naphthalimide fluorescence), blue/green (naphthalimide excimer) and red (Eu) components. In the solid state H_3L gives white emission on its own due to aggregation effects broadening the luminescence spectrum such that its emission is panchromatic.

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Notes and references

‡ CCT = Correlated Colour Temperature.

§ Quantum yield for Eu-based emission estimated from $\Phi = \tau/\tau_n$ where $\tau = 1.1$ ms and, $\tau_n =$ the "natural" radiative lifetime of 9.5 ms (ref. 12).

¶ Time-resolved measurements show that this broad luminescence has three decay components with lifetimes of 20 ns, 250 ns and 4.5 µs; the first two of these can reasonably be ascribed to excimer-type fluorescence from naphthalimide units in different aggregation states, and the 4.5 µs second (which was a very small contributor) could be a trace of phosphorescence from the triplet state.

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