Thermally stable zinc disalphen macrocycles showing solid state and aggregation induced enhanced emission (AIEE)

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ABSTRACT: In order to investigate the solid-state light emission of zinc salphen macrocycle complexes, 7 dinuclear zinc salphen macrocycle complexes (1 – 7), with acetate or hexanoate co-ligands, are synthesised. The complexes are stable in air up to 300 °C, as shown via thermogravimetric analysis (TGA), and exhibit green to orange-red emission in solution (λ_{em} = 550 – 600 nm, PLQE ≤ 1 %), and slightly enhanced yellow to orange-red emission in the solid state (λ_{em} = 570 – 625 nm, PLQE = 1 – 5 %). Complexes **1**, **2**, **4**, **5**, and **7** also display aggregation induced enhanced emission (AIEE) when hexane (a non-solvent) is added to a chloroform solution of the complexes, with complex **4** displaying a 75-fold increase in peak emission intensity upon aggregation (in 0.25:0.75 chloroform: n-hexane mixture).

Introduction

Metal salen complexes have been extensively studied in catalysis,[1] as have the related metal salphen complexes,[1-2] primarily due to their high activity and selectivity across a wide range of chemical reactions. Many salen[3] and salphen complexes[4] are known to display emission within the visible spectrum. In particular, aluminium salens [3i, 5] have shown blue-green emission, with solution photoluminescence quantum efficiencies (PLQEs) up to 40 %, and thin film PLQEs up to 24 %. Aluminium salen complexes have also been employed as suitable host materials[6] and hole blocking layers[7] in organic light emitting diodes (OLEDs), demonstrating their facility to transport charges effectively within electronic devices. Some platinum salens[3d, 3e] have shown yellow-red emission (solution PLQEs up to 27 %) and have been investigated as emitters within OLEDs, the best performing device within that study displaying an efficiency of 31 cd A^{-1} and a device lifetime of up to 77,000 hours at 500 cd m^{-2}.

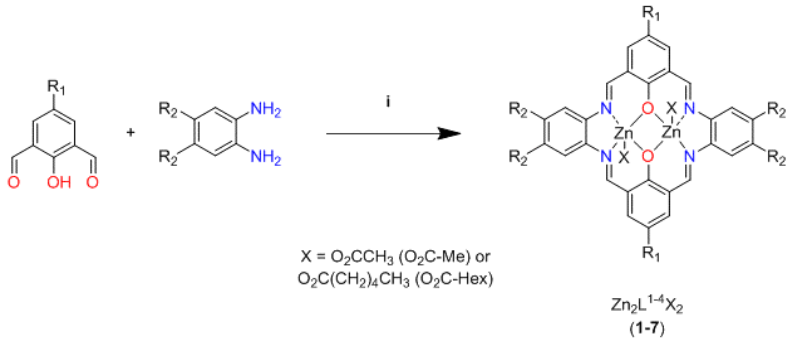
Salphen complexes are less prevalent in catalysis than salen complexes, and have extended electronic conjugation and higher rigidity. Salphens have so far shown greater promise for applications in fields such as sensing and electronics. For example they have been used as building blocks in supramolecular chemistry,[8] as columnar liquid crystals,[9] and in the electronic modification of carbon nanotubes.[10] They have also proven to be useful optical sensors, such as in their binding to DNA;[11] detection of nitro compounds by the quenching of their fluorescence;[3g, 4d] the sensing of lead ions;[4b] and as receptors for various anions,[12] to highlight just a few selected examples.

There have been several reviews on the synthesis and applications of these types of π-conjugated systems and related salphen compounds,[13] detailing their versatility and the scope for further research into their properties. Zinc salphens are particularly interesting, as a range of mono-,[3g, 4d, 8d, 14] di-,[4a, 13, 15] and multi-nuclear[13, 15a, 16] compounds can readily be isolated. In addition, zinc is a widely available, inexpensive metal, and thus compounds of zinc are desirable substitutes for compounds of rare metals, such as iridium and platinum, which remain common in optoelectronic devices.[11b, 17]

Aggregation induced enhanced emission (AIEE)[18] is a phenomenon in which the photoluminescence quantum efficiency (PLQE) of a substance is enhanced when its molecules are aggregated.[4c, 19] AIEE is essentially the opposite effect to aggregation caused quenching (ACQ) - common in laser dyes and other light-emitting materials - and increasingly many new chemical compounds are being discovered or designed to display it.[18, 20] Some organic salen-based gel systems[4c] and salen ligands,[19e] have also been identified as AIEE materials, among which several have been applied in organic optoelectronic devices, as fluorescent probes, and for cell imaging.

The emission enhancement in salen based gel systems has been attributed to the formation of J-aggregates, which help to

Scheme 1. Generic reaction scheme for the formation of zinc salphen macrocyclic complexes (1-7).



Entry	L	R_1	R_2	X	Yield / %
1	L^1	t-Bu	H	O_2C-Me	81
2	L^2	t-Bu	Me	O_2C-Me	70
3	L^3	NO_2	H	O_2C-Me	67
4	L^1	t-Bu	H	O_2C-Hex	54
5	L^2	t-Bu	Me	O_2C-Hex	85
6	L^3	NO_2	H	O_2C-Hex	48
7	L^4	t-Bu	$OCH_2C(CH_3)_3$	O_2C-Me	23

(i) 2 equivalents of zinc acetate dihydrate or zinc (bis)hexanoate, methanol/ chloroform, reflux, 6-18 h.

prevent intramolecular rotations in these compounds.[4c] In a recent and extensive study on AIEE-active salen ligands,[19e] several strong non-covalent intermolecular interactions (H···π, H···H, O···H, and N···H) and weak intermolecular face-to-face π-π interactions were suggested to be important.Enhanced solid state PLQEs of up to 75 % were reported, whilst in solution many of the salen compounds had PLQEs of less than 1 % (the highest solution PLQE was 10 %). AIEE has also been demonstrated with salicylaldehyde-azine functionalised materials,[19b, 19f, 19g] which are structurally similar to salens and salphens. These organic compounds have made use of AIEE mechanisms and may be useful for hydrazine detection,[19g] and as fluorescent pH probes.[19f]

There are far fewer reports of metal complexes that display AIEE,[14c, 19b, 21] compared with the large library of organic AIEE materials.[18, 20] However, as the melting and decomposition temperatures of metal complexes are typically greater than organic compounds, thermally stable metal complexes that display AIEE are desirable for processes or applications that subject the materials to higher temperatures (e.g. > 200 °C). In fact in one report the AIEE properties and thermal stability of salicylaldehyde-azine containing ligands were both improved upon complexation with small quantities (up to 4 wt%) of zinc(II) ions.[19b] The thermal stability and AIEE properties of similar zinc based compounds may therefore prove useful for future applications.

Salphen macrocycle complexes were targeted as they have high levels of conjugation, and show precedent for light emission (*vide infra*). Whilst macrocyclic salen and salphen structures are well documented,[13b, 15b, 16, 22] there are fewer examples of the smaller [2+2] disalphen macrocycles,[15b, 22a, 22b, 23] although some patents claim applications as electrode catalysts for fuel cells[24] and batteries.[25]

[2+2] zinc disalphen macrocycles, with chloride and nitrate co-ligands, have previously been reported as green emitters in DMSO solution, displaying 2 distinct peaks at 480 nm and 521 nm (with chloro co-ligands), and at 480 nm and 527 nm (with nitro co-ligands).[15b, 23e] The absorption bands were assigned to metal to ligand charge transfer (MLCT) (d → π*) transitions due to the relatively high extinction coefficients (1.9 – 2.9 x 10^4 $M^{-1}cm^{-1}$). The zinc disalphen macrocycles displayed fluorescence lifetimes in solution of 650 ps and 480 ps, and were emissive in the solid state with red-shifted emission spectra (λ_{em} = 565 and 575 nm).[15b] However, no efficiency data was provided for the solution or solid state emission.

In a separate study, the high and low energy absorptions of a zinc disalphen macrocycle, with nitro co-ligands, were assigned as ligand centered (LC) n→π* and MLCT bands respectively,[23e] with emission being observed at 500 nm. Zinc disalphen macrocycles showed red-shifted emission compared to the zinc disalen macrocycles that were investigated. The PLQE of the zinc disalphen was 14.3 % in DMSO/water, significantly higher than that of the zinc disalen macrocycle complexes (PLQEs = 3.0 – 8.4 %). However, there was no reporting of the solid state PLQEs of these compounds.

To the best of our knowledge, there have not yet been any reports on the light emission properties of [2+2] zinc disalphen macrocycles with carboxylate co-ligands, and more generally no reports have indicated the existence of AIEE phenomena for such macrocycles. In addition, knowledge of solid state PLQEs is required for the development of solid-state devices.

Here, a series of new [2+2] zinc salphen macrocycle complexes is prepared and their electronic and photophysical properties investigated, including their PLQEs in both solution and solid state. The results indicate that AIEE can indeed occur for zinc disalphen macrocycles.

Results and Discussion

Synthesis. 7 Zinc disalphen macrocycle complexes, with acetate (**1 – 3**, and **7**) or hexanoate co-ligands (**4 – 6**), were synthesised in moderate to good yields (23 – 81 %, **Scheme 1**). The reactions were all carried out under aerobic conditions, except for complex **7**, due to the instability of the diamine starting material.[16] The formation of the macrocyclic products required high dilution conditions and slow addition of the diamine reagent.

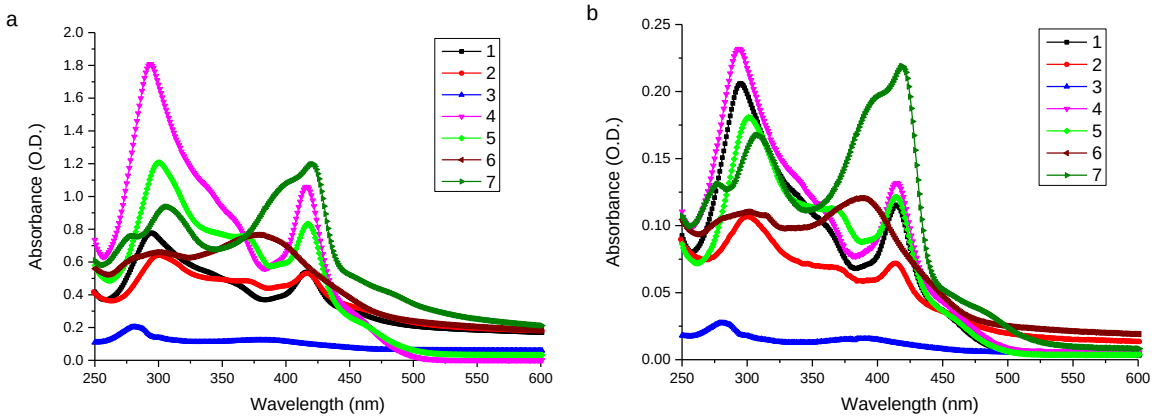


Figure 1. (a) The absorption spectra of complexes **1** – **7** in acetonitrile solution at 4.0 – 5.6 x 10^{-5} M and (b) 5.0 – 7.0 x 10^{-6} M concentration.

The crude complexes were readily isolated via filtration of the reaction mixture after cooling to ambient temperature. Analytically pure complexes were obtained after recrystallisation from chloroform/diethyl ether (complexes **1**, **2**, **4** and **5**) or chloroform/hexane (complex **7**), whereas complexes **3** and **6** were analytically pure after filtration. All of the complexes were air stable up to at least 300 °C as shown via thermogravimetric analysis (TGA) (**S34** – **S340**, **ESI**).

The isolated complexes were either amorphous or microcrystalline powders, and were characterised by ^{1}H NMR, mass spectrometry, and elemental analysis, providing clear evidence for the formation of the fully conjugated, macrocyclic products in high purity (see **ESI**).

The ^{1}H NMR spectra (**S1** – **S5**, **ESI**) of complexes **1**, **2**, **4**, **5**, and **7** were obtained for d-chloroform solutions. Useful information was difficult to obtain, however, for complexes **3** and **6**, due to their low solubilities in $CDCl_3$ and also in d-DMSO.

Where ^{1}H NMR spectra could be obtained, a characteristic signal for the imine protons was observed at around 9 ppm (integration of 4), along with the expected aromatic signals between 7-8 ppm. The *tert*-butyl signals were observed at ~1.4 ppm for complexes **1**, **2**, **4**, **5** and **7** in addition to the characteristic signals of coordinated acetate or hexanoate co-ligands, all with the expected integration ratios. A weak ^{13}C NMR spectrum of complex **7** could be recorded in $CDCl_3$, and all carbons containing C-H bonds could be assigned via a HSQC experiment (**S6**, **ESI**). The solubilities of complexes **1** – **6** were too low to obtain useful ^{13}C spectra.

Absorption Spectroscopy. The absorption spectra of the complexes were recorded in acetonitrile (**Figure 1** and **S7** – **S10**, **ESI)**. The lowest energy absorptions were between 380 – 480 nm, and are tentatively assigned to MLCT transitions based on the extinction coefficients (ε) (**T1, ESI**). Light scattering was observed with most of the spectra in acetonitrile solution, even at a range of concentrations (**Figure 1** and **S7** – **S10**, **ESI**), suggesting the presence of aggregates rather than just isolated molecular species. For complexes **1**, **2**, **4**, **5**, and **7**, it is likely that a combination of isolated molecular species, J-, and H-aggregates are present. This is seen within the literature for other molecular materials that form H- and J-aggregates, resulting in additional absorptions at higher and lower energies, respectively, compared with the isolated molecular species.[26] This may also be the case for complexes **3** and **6**, however their spectra were relatively broad and featureless, and therefore more difficult to assign.

The spectra of complexes **1 – 7** had two major peak maxima, both of which are assigned to the isolated molecular species on the basis that they change little with dilution (c.f. Figures 1(a) and (b)). The higher energy absorptions occur between 293 – 307 nm, whereas the lower energy absorptions occur between 380 – 420 nm. The absorption features found between these maxima may then be attributed to the presence of H-aggregates, whereas the absorptions that are observed as shoulders at lower energies (> 420 nm) are attributed to J-aggregates. As expected, these latter absorptions do noticeably decrease in relative intensity upon dilution.

The high energy absorptions of complexes **1** and **4** occurred at 294 nm, whereas a bathochromic shift for complexes **2** and **5** occurred due to the introduction of methyl substituents in the R_2 position. A further bathochromic shift was observed to 307 nm when the methyl groups were replaced with neopentoxy groups, as in complex **7**.

The lower energy absorptions of complexes **1**, **2**, **4**, and **5** were all the same at ~417 nm, whereas for complex **7** (**Figure 1a** and **S10, ESI**) a bathochromic shift to 420 nm was observed. In contrast, hypsochromic shifts in the absorption spectra of complexes **3** and **6** (**Figure 1** and **S9**, **ESI**) were detected, with absorption maxima at 380 nm for the lowest energy transitions.

From the absorption spectra of all the complexes it is clear that the presence of electron withdrawing groups in the R_1 position shifts the absorption spectra to higher energies, whereas the presence of electron donating groups in the R_2 position shifts the spectra to lower energies.

There was no obvious trend observed in the absorption spectra with the different co-ligands (acetate or hexanoate), and the results suggest that they have no, or only minimal, effects on the optical gap of the complexes. However, the difference in carbon chain lengths of the co-ligands may have subtle effects on the arrangement of various aggregation states. This may explain the differences in the absorption spectra between the complexes, at various concentrations, and the

degree of change in the relative populations of isolated molecules, and H- and J-aggregates.

Solution Emission. All of the complexes emit light in both acetonitrile (**Figure 2**, **S11 – S14**, **ESI**) and chloroform solution on excitation into the lowest energy absorption bands with a halogen light source (λ_{ex} = 390 – 425 nm). In acetonitrile solution, the peak maxima (λ_{max}) range from 530 – 600 nm (**Figure 2**). Broad green emission at λ_{max} = 550 – 560 nm was observed from complexes **1**, **2**, **4**, and **5**, and a distinctive hypsochromic shift in the emission wavelength by 10 – 20 nm on dilution from 10^{-5} M to 10^{-6} M concentration was noted (**S11** – **S12**, **ESI**). This observation can be explained by a relative reduction in J-aggregate and a relative increase in isolated molecular species emission on dilution.

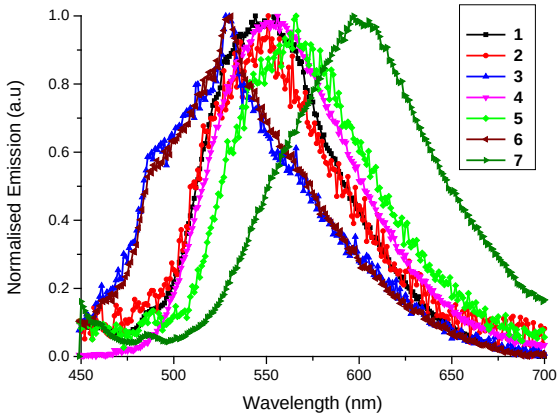


Figure 2: Normalised emission spectra of complexes **1** – **7** in acetonitrile solution at 4.0 – 5.6 x 10^{-5} M concentrations, λ_{ex} = 390 – 425 nm.

The emission spectra of complexes **3** and **6** in acetonitrile solution (**Figure 2** and **ESI**) were blue-shifted compared to the other complexes, with a sharp peak at 530 nm, and broad emission from 450 – 650 nm. The intensities of the sharp peaks decreased on dilution and a slight hypsochromic shift from 530 nm to 525 nm (**S9**, **ESI**) was observed, again likely due to the reduction in the number of J-aggregates.

The emission spectrum of complex **7** in acetonitrile solution (**Figure 2** and **S14**, **ESI**) displayed a bathochromic shift compared to all other complexes, with a broad emission maximum at 600 nm, and a vibronic shoulder at ~ 560 nm that mirrored the structure in the corresponding absorption spectrum.

The solution PLQEs of complexes **1**, **2**, **4**, **5** and **7** were determined in chloroform using fluorescein as an internal standard (**S19** – **S25**, **ESI**). This gave values of ~ 1 % or lower for each of the complexes (**Table 1**). These low values may be explained by the absence, or low population, of J-aggregates, combined with the relative increase in isolated molecular species, which can more readily relax to the ground state via vibrational energy dissipation.

Solution Excitation Spectroscopy. In order to further test the hypothesis that the presence of J-aggregates helps to improve the emission of the zinc macrocycle complexes, the excitation spectra of the complexes were recorded at high (4.0 x 10^{-5} M) and low concentrations (1.3 x 10^{-6} M) (**S15 – S18**, **ESI**). The results clearly indicate that, at the higher concentration, light emission intensities (at λ_{em} = 530 – 600 nm) are retained when the excitation wavelength is moved to the longer wavelengths that correspond to J-aggregate absorption (> 420 nm for complexes **1**, **2**, **4**, and **5**, > 425 nm for complex **7**, and > 400 nm for complexes **3** and **6**). These effects are particularly prominent for complexes **2**, **4**, **5**, and **7**. In addition, following dilution to 1.3 x 10^{-6} M concentration the longer-wavelength-excited light emission for each of the complexes decreases, just as expected for a reduction in J-aggregate population.

The excitation spectra for complex **7** at high (4.0 x 10^{-5} M) and low (1.3 x 10^{-6} M) concentration (**S18**, **ESI**) show these effects very clearly. At high concentration, the emission (λ_{em} = 600 nm) does not begin to fall rapidly until the excitation wavelength exceeds ~500 nm, whereas at low concentration the emission intensity decreases rapidly at excitation wavelengths greater than ~425 nm.

Solid State Emission. The solid state emission spectra of complexes **1**, **2**, **4**, **5**, and **7** (**Figure 3** and **S26** – **S28**, **ESI**) were recorded using the analytically pure powders, all displaying bathochromic shifts by varying extents to the solution emission spectra, yielding bright yellow to orange-red emissions (peak maxima ranging from 569 nm to 630 nm). The solid-state emission from complexes **3** and **6** were not recorded as the emission intensities were significantly lower than for the other complexes.

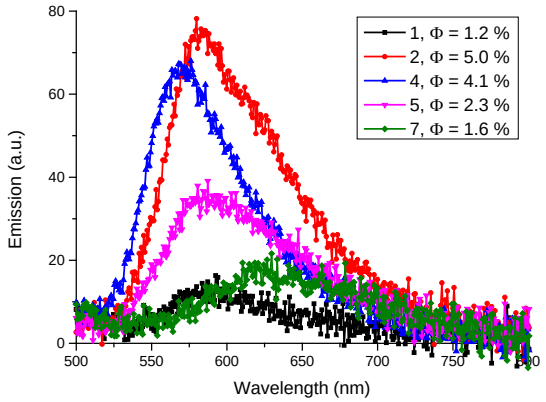


Figure 3: Emission spectra of complexes **1**, **2**, **4**, **5**, and **7** in the solid state (as powders), λ_{ex} = 440 nm.

Table 1. PLQE values of complexes 1-7.

Entry	Solution PLQE[a] / %	Solid State PLQE[b] / %
1	1.1	1.2
2	0.64	5.0
3	-	-
4	0.76	4.1
5	1.0	2.3
6	-	-
7	1.0	1.6

a: determined using a fluorescein standard; b: determined using an integrating sphere (details in **ESI**).

The solid state PLQEs of the complexes **1**, **2**, **4**, **5**, and **7** are all slightly enhanced when compared to the solution PLQEs (**Table 1**), although this effect is minimal with complex **1**. The largest difference was for complexes **2** and **4**, which had solid state PLQEs that were higher than the solution PLQEs by a factor of ~8 and ~5 respectively. The reduction in excited state non-radiative decay in the solid state is most likely due to the presence of intermolecular interactions which restrict rotations and/or vibrations that otherwise dissipate energy or stabilize charge separation. Such behavior is common in materials that exhibit AIEE.

Aggregation Induced Enhanced Emission (AIEE). To further investigate AIEE, **1**, **2**, **4**, **5**, and **7** were completely dissolved in chloroform, producing clear yellow solutions. The non-solvent n-hexane was then added in portions to induce clearly visible aggregation; the clear solutions became increasingly turbid. The emission spectra were recorded after each sequential addition of n-hexane. Pure chloroform solutions exhibited only very-weak light emission but the intensities increased significantly upon hexane-induced aggregation (**Figure 4**, **S29** and **S30**, **ESI**). Complexes **3** and **6** were of insufficient solubility in chloroform for AIEE to be successfully studied (**S31**, **ESI**) with this solvent system.

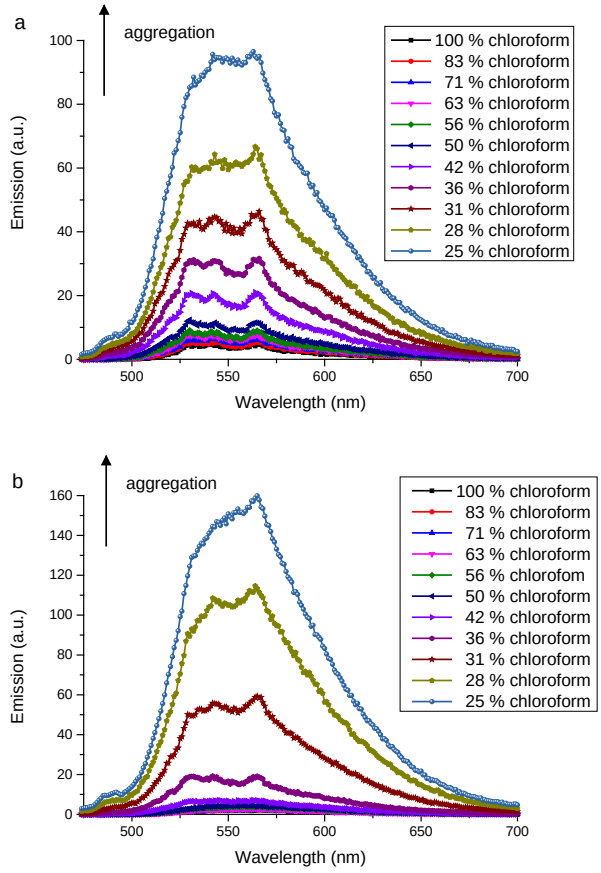


Figure 4: Emission spectra (λ_{ex} = 415 nm) of complexes **2** (a) and **4** (b) for different chloroform (25 – 100 %): n-hexane mixtures.

Complexes **2** and **4** showed the greatest change in emission intensity upon n-hexane addition, consistent with the observed increases in PLQE between solution and solid-state samples. The emission intensities increased 19-fold for **2** and 75-fold for **4** on progressing from the pure (100%) chloroform solution to a 25% : 75% chloroform : n-hexane mixture (**Figure 4**), the latter being the largest increase out of the complexes studied. Aggregation of the complexes was typically visible in the mixture range between 25 and 50 % chloroform for **1**, **2**, **4**, and **5**. A larger proportion of n-hexane was required to induce aggregation for **7** (**S30**, **ESI**), due to its higher solubility in chloroform. Even then, a gradual increase in the emission intensity could still be observed on addition of non-solvent, and aggregation became clear once the chloroform fraction had fallen to 13 %.

The PLQE values of complexes **4** and **5** were obtained at various compositions of chloroform: n-hexane (as shown in **S32 – S33**, **ESI**) as their aggregates remained suspended in the mixtures for long enough to conduct the experiments using an integrating sphere. The results provide further evidence of AIEE, producing PLQE values of 0.2 % and 1.6 % in pure chloroform respectively, which increased upon aggregation to 5.5 % and 4.8 % in 20 % chloroform: n-hexane solvent.

The PLQE values of the aggregated species were difficult to obtain for complexes **1**, **2**, and **7** (all of which have acetate co-ligands) as sedimentation rapidly occurred in the time required to set-up samples within the integrating sphere. This sedimentation likely prevented the incident excitation beam from hitting the aggregates of these complexes. This sedimentation did not occur as rapidly with complexes **4** and **5**, most likely due to their hexanoate co-ligands, which could interact with the n-hexane co-solvent.

The increase in emission intensity upon aggregation for complexes **1**, **2**, **4**, **5**, and **7** demonstrates that these materials do indeed exhibit AIEE - the first zinc disalphen macrocycle complexes reported to do so. The substantial enhancement in their light emission, particularly for complexes **2, 4** and **5** offers, additionally, the prospect of a new class of AIEE molecules of interest for applications including sensing.

Conclusions

The syntheses and isolation of several new [2+2] zinc disalphen macrocycle complexes was achieved. The compounds are emissive in acetonitrile and chloroform solution (green to orange, PLQEs ≤ 1 %), and in the solid state (yellow to orange-red). Complexes **2**, **4**, **5**, and **7** all displayed higher PLQEs (2 – 5 %) in the solid state, with complex **2** showing the largest emission enhancement; its PLQE increased by a factor of 8. The emission intensities of complexes **1**, **2**, **4**, **5**, and **7** all increased significantly upon aggregation in chloroform: hexane solvent mixtures, with complex **4** displaying the largest enhancement (75-fold).

The lack of self-quenching for these complexes in concentrated solution, and the enhancement of their emission in the solid state, and when aggregated, are typical observations for molecules that exhibit AIEE. The ease with which these complexes can be isolated, their tunable electronic structures, and their good air and temperature (> 300 °C) stabilities may make these new materials useful for processes and applications that may not be accessible for previous organic AIEE materials, which have tended to possess low melting and decomposition temperatures.

The PLQE values of these complexes are currently too low for them to be readily used as emitting materials in OLEDs. However, they might find application in sensors for various chemical or biological species. Ligand design changes could also be introduced should aqueous solubility be required, for example in medical imaging or biological applications. How this would affect their light emitting properties remains unclear. Further modification of the ligand structure, or co-ligands, may also allow for PLQE enhancement or for further tuning of the light emission to produce deep-red or near-infrared (NIR) emitters. Work remains on-going to investigate other dinuclear and multinuclear zinc salphen complexes, their photophysical properties, and potential applications.

ASSOCIATED CONTENT

Supporting Information.
The complete experimental procedures and characterisation data.
TGA data, additional absorption and light emission spectra, including excitation spectra, data for determination of the PLQE values and AIEE experiments.
This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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ABBREVIATIONS

AIEE, aggregation induced enhanced emission, PLQE, photo-luminescence quantum efficiency, TGA, thermogravimetric analysis, DMSO, dimethylsulfoxide, NIR, near infra-red.

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Graphical Abstract for:

Thermally stable zinc disalphen macrocycles showing solid state and aggregation induced enhanced emission (AIEE)

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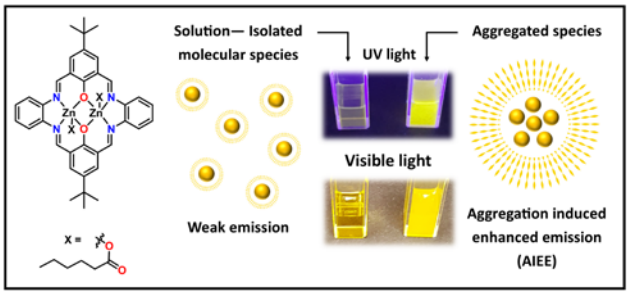

TOC synopsis

A series of seven dinuclear zinc salphen macrocycle complexes are weakly photoemissive in solution, whilst some complexes show aggregation induced emission in the solid state.