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A saponification-triggered gelation of ester-based Zn(II) complex through conformational transformations†

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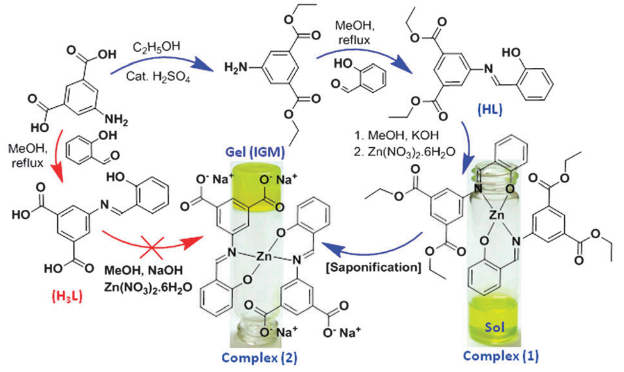
Novel saponification-triggered gelation in an ester-based bis-salen Zn(II) complex (1) is described. Strategic structural modifications induced by NaOH in 1 tune the dipolar-/π-interactions leading to J-aggregation and the creation of an inorganic gel material (IGM), which has been established by photophysical, DFT and rheological studies.

Gel chemistry has attracted remarkable attention over the past couple of decades, because of the significant contributions gel materials can make in diverse areas.[1] Due to their fascinating structures and usage, numerous methodologies, including sonication, photo-chemical, pH, temperature and analyte-assisted approaches have been developed for the synthesis of gel materials, particularly from low-molecular-weight gelators called LMWGs.[1b,2] In addition, gelation properties and the potential use of the LMWGs are usually fine-tuned by their design and molecular architecture *via* alteration of the non-covalent/weak (π-stacking, H-bonding, hydrophobic and dipole–dipole) interactions.

Usually, gelators create gels in an appropriate solvent or solvent mixture, sometimes with the addition of an additive for the optimization of gelation behavior, such as metals, forming metal–organic gels (MOGs).[3] However, to date, no rational methods for the creation of MOGs directly from an inorganic complex *via* a chemical transformation have yet been reported. Moreover, the gelation properties of 'ether/ester'-based LMWGs are often optimized by creating alterations in the alkyl chain through a sophisticated multi-step synthesis.[1c,4] These issues motivated us to develop an improved, single-step, convenient and cost-effective gelation process for such systems. Furthermore, peripherally substituted ether/ester(s) are suitable for gelation, and indeed, the phenyl ring of the salen unit may favour this process by increasing the planar π-interactions.[1b] Considering these points, the ligand (**HL**), which has two *m*-substituted ethyl ester groups and a simple salen core on an isophthalate ring, was chosen for the present study, and thus a zinc complex [Zn(L$_2$)] (**1**) imparting **L**$^-$ was prepared. The complex **1** exhibits excellent photophysical properties and greater tunability for planar π-interactions owing to the presence of two **L**$^-$ units. Through this contribution, we demonstrate the gelation in **1** triggered by saponification. To our knowledge, this is the first report detailing the gelation of an inorganic complex (MOG) produced by saponification.

Complex **1** is soluble in weakly polar aprotic solvents like CHCl$_3$, THF and DCM, but it does not form a gel. It requires an additive to enforce the appropriate conformational changes to facilitate the π–π/weak interactions for the gelation to occur. To work out this strategy, saponification, typically employed for the hydrolysis of fatty acid esters into –COO$^-$Na$^+$/–K$^+$ salts in the presence of NaOH/–KOH, has been undertaken with a slight modification. Herein, NaOH has been used to convert the esters of **1** into highly '*polar groups*' (in the *least polar* solvent, CHCl$_3$) to facilitate significant conformational changes suitable for gel phase oriented weak π-interactions, and in turn gelation (Scheme 1).[1a] Moreover, methanolic instead of an aqueous solution of NaOH has been employed to avoid possible hydrolysis of the aldimine moiety and to hold the basic skeleton of the molecule intact,



Scheme 1 Synthetic strategy adopted for **IGM** demonstrating the creation of **IGM** from complex **1**.

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and also to address the miscibility criterion. Furthermore, the end product, which forms the gel, is a bis-salen Zn(II) complex with four $-COO^{-}Na^{+}$ moieties (**2**). All the attempts to synthesize **2** directly by reacting unprotected ligand (**H_3L**) with metal salts failed; moreover, such a reaction always afforded only an insoluble product (Scheme 1, red arrowed pathway).

The addition of methanolic NaOH (2.0 M) to a solution of **1** in $CHCl_3$ afforded **IGM** at rt (1.4%, w/v) (Fig. S1, ESI†). The gelation was also scrutinized using other common solvents with the resulting data given in Table S1, ESI.† Complexes based on Cd^{2+}, Cu^{2+}, Co^{2+} and Ni^{2+} were also synthesized under analogous conditions, and it was observed that these afforded a gelatinous precipitate, except for Cd^{2+}, which required a longer gelation time (Fig. S2, ESI†). The gelation of **1** was examined with other bases, namely, NH_3, Et_3N, $LiOH{\cdot}H_2O$, KOH and CsOH, but it only occurred with Na^{+}/K^{+} and not with Li^{+}/other bases. The inability of Li^{+} to induce gelation may be attributed to $>C{=}O{\cdots}Li^{+}$ interactions, as evidenced by a shift of the $>C{=}O\nu_{str}$ band (~9 cm^{-1}) in the vibrational spectra of **1** on the addition of $LiOH{\cdot}H_2O$ (Fig. S5, ESI†).[5] This observation strongly indicates that gelation is governed by saponification. Under heating and cooling, the **IGM** showed thermoreversibility up to ~63 °C.

Technically, saponification may create a mixture of Na^{+}-salt, due to several ester sites on **1**. Therefore, it has been optimized by varying the ratio of **1** : NaOH (*i.e.* 1 : 1 to 1 : 6), and it was established that 1 : 4 is the most appropriate ratio for a strong gel (based on creating a compact and transparent gel in the minimum time, Fig. S2, ESI†), which indirectly signified saponification as the basis for gelation. Morphology of the **IGM** was followed by scanning electron microscopy, which revealed aggregated gel fibres that were further confirmed by AFM images. TEM images of the diluted gel (~10^{-4} M) indicated intermediate assembly, as evident from the aggregated nano-sized structures exhibiting some fibre like directional alignments (Fig. S3 and S4, ESI†).[2a]

To gain a deeper insight into the gelation mechanism, UV/vis and fluorescence studies were undertaken (ESI†). The addition of NaOH to a solution of **1** (c, 5.0 × 10^{-5} M) leads to a bathochromic shift ($\Delta\lambda$, 41 nm) and the appearance of a new band at 384 nm. Moreover, there was a concurrent decrease in the optical density of the characteristic bands due to **1** (λ, 343 and 275 nm) (Fig. S6, ESI†). The band at 384 nm may be ascribed to the creation of a new species by cleavage of the ester linkages after saponification (complex **2**). Ratiometric changes were observed with a noticeable isosbestic point at ~364 nm, which signifies the formation of **2** by the gradual degradation of **1**. A large bathochromic shift (41 nm) indicates appreciable conformational changes leading to J-aggregation *via* π-stacking (Fig. 1a).[6a] This observation was supported by variable temperature (VT) UV/vis measurements on diluted gel, which showed a significant hypo- and hypso-chromic shift (~10 nm) in the absorption band associated with aggregation (~384 nm) (Fig. S6c, ESI†).[6b]

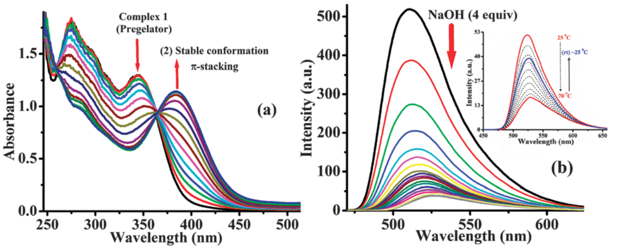

Fig. 1 (a) UV/vis titration spectra of **1** (c, 5.0 × 10^{-5} M in $CHCl_3$) *vs.* NaOH; (b) fluorescence titration spectra of **1** (c, 2.0 × 10^{-2} M in $CHCl_3$) *vs.* NaOH. Inset shows the variable temperature spectra of **IGM** (λ_{em} = 526 nm), exploring the AIEE effect and showing the ~80% thermoreversibility.

The fluorescence spectrum of **1** (c, 1.0 × 10^{-2} M) displayed a strong band at 510 nm (λ_{ex}, 343 nm; Stokes shift, ~165 nm) (Fig. S7a, ESI†). Aliquot additions of NaOH resulted in significant quenching, followed by a gradual red shift (~16 nm, at saturation; limit of quantification, ~1.0 : 0.2 to ~1.0 : 4.0 for **1** : NaOH; Fig. 1b). These spectral changes signify the conversion of **1** into **2** and the appreciable conformational changes pertaining to it with a π-stacking like excimer formation. The decrease in the fluorescence intensity may be attributed to the enhanced excitation energy transfer within and/or between the stacked species, *i.e.* self-quenching. Furthermore, the small increase in the fluorescence intensity observed during the last few additions of NaOH may be associated with various weak interactions in the gel matrix (due to solvated Na^{+} ions and $-COO^{-}$ polar groups), attributable to an aggregation-induced emission enhancement (AIEE) effect (Fig. S7c, ESI†).[5a] Fluorescence studies established the existence of the remarkable conformational changes leading to J-aggregates and are consistent with the conclusions drawn from the UV/vis studies. The spectral studies carried out at high concentrations were well optimized and their authenticity justified by other experiments (Fig. S7, ESI†). Variable temperature fluorescence experiments on **IGM** displayed a continual decrease of the fluorescence intensity in the temperature range 25–70 °C, attributable to segregation of the aggregates. Based on only an insignificant shift in the position of the bands, any definite change in the conformation may be ruled out. Furthermore, upon cooling to rt (~25 °C), the intensity regained much of its initial value (~80%), which indicates the re-aggregation (Fig. 1b). These observations strongly indicate the thermoreversible nature of the **IGM** and also the AIEE effect, due to the repeated segregation and re-aggregation in the gel matrix.

To achieve clear mechanistic insights and also to have an idea about the formation of the aggregates, ^{1}H NMR titration was carried out by taking **1** in $CDCl_3$ (0.02 M), NaOH in CD_3OD (2.0 M), and adding NaOH in four steps (1.0 equiv. each). It was observed that the isophthalate ring protons $H\underline{1}$ (2H, δ 8.46 ppm) displayed a significant downfield shift ($\Delta\delta$, 0.16), which most likely indicated π-stacking and/or cation–π interactions due to the presence of Na^{+} ions. The resonance corresponding to proton $H\underline{1}$ displayed a criss-cross over the aldimine signal $H\underline{4}$ (2H, δ 8.49 ppm), which does not indicate any shift. It simply indicates that the added NaOH does not hydrolyse the confined aldimine moiety. The criss-crossing was further affirmed by the merger of both the signals ($H\underline{1}$ and $H\underline{4}$) into a single broad peak after the addition of 1.0 equiv. of NaOH and the separation upon further additions (2.0–4.0 equiv.) of the base. Furthermore, the *H2* and *H3* (4H, δ 8.00 ppm) protons from the same ring may not be involved in stacking, as these hardly exhibited any shift. Moreover, amongst phenolate ring protons (8H; *H5*, *H6*, *H7* and *H8*, δ 7.44–6.66 ppm) only *H6* and *H8* (*o*- and *p*- to phenolate oxygen) displayed an upfield shift with broad features. This may be due to their involvement in C–H$\cdots\pi$ type interactions.[6b,7] The concomitant disappearance of signals in the aliphatic region corroborated well with cleavage of the ester linkage (–CH_2–, 8H; *H9* and *H11*, δ 4.28 ppm and –CH_3, 12H; *H10* and *H12*, δ 1.28 ppm) (Fig. S8, ESI†). Involvement of the *H1* in π-stacking was confirmed by a VT ^{1}H NMR experiment, as it successively exhibited a high field shift ($\Delta\delta$, 0.09) at 55 °C. Thus, the NMR studies undoubtedly demonstrated the conversion of esters into a carboxylate moiety (**1** → **2**) with an appropriate conformation for π-interactions favourable for aggregation, and consecutively, for gelation.

To firmly validate the significant conformational reorganization, DFT optimizations were undertaken on the model structures of **1** and **2**. The optimized structures clearly showed substantial geometrical differences from the square planar (**1**) to the tetrahedral (**2**) (Fig. S9, ESI†). Distant isophthalate rings in **1** (like the Cu^{2+} analogue reported in our previous work) are close to each other in **2**.[8] In doing so, **1** might have undergone significant conformational changes, most likely by an enormous increase (~185 fold) in the dipole moment due to the –COO^-Na^+ moiety. Two Na^+ ions are flanked with the –COO^- moieties of the native isophthalate rings, while the other two are flanked by the –COO^- of both isophthalate rings. Na^+ ions are also involved in significant interactions with the subsequent isophthalate rings, which provide strong evidence of the dominant cation–π interactions (2.13–2.76 Å). The optimized structure of **2** favours π–π stacking interactions involving isophthalate rings, even after involvement of the Na^+ ion in close proximity, and thereby supports the downfield shift for the *H1* proton. Moreover, it confirms the intermolecular π-interactions that are indispensable for gelation due to the position of the fourth Na^+, which is most probably involved in interplanar cation–π interactions. On the contrary, phenolate rings are distant enough that they can only get involved in stabilization of the supramolecular network (gel matrix) *via* weak C–H$\cdots\pi$ interactions for aggregation, and therefore support unusual chemical shifts for the phenolate ring protons (*H6* and *H8*). Thus, the conclusions drawn from the spectral studies are consistent with the observations elicited from the DFT-optimized structures (Fig. 2a). The inability of Cu^{2+}, Ni^{2+} and Co^{2+} analogues to form a gel can also be explained by performing DFT calculations (Fig. S9, ESI†).

To exclude the artefacts of the gel phase material, freshly prepared **IGM** was directly subjected to rheological studies. At fixed concentrations of **IGM** (1.4%, w/v), the storage (G') and loss modulus (G'') were measured in the temperature range 22–100 °C, and it was observed that $G' > G''$ up to 84 °C. The gel started to deform at 70 °C and ended at 84 °C, where both the moduli meet each other ($G' = G''$), suggesting a phase transformation. A sharp change in the loss tangent value ($\tan\delta = G''/G'$) at 84 °C specifies T_{gel} for **IGM** (Fig. 2b).[5b]

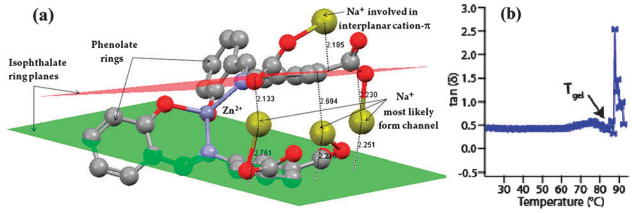

Fig. 2 (a) DFT-optimized structure of **2** showing the involvement of the isophthalate ring planes in π–π/cation–π interactions; (b) dynamic temperature ramp of the loss of tangent ($\tan\delta = G''/G'$) at 5 °C min^{-1}, showing the phase transition temperature (T_{gel}) 84 °C for gel.

Complex viscosity measurements at increasing temperature supported the phase transition at 80 °C. This shows phase transition *via gel–semi sol–solid*, which is expected for a mixed solvent-based inorganic gel, and it indicates formation of a typical '*soft-solid*' like gel phase material. This observation is consistent with the VT fluorescence studies. A double logarithmic plot between the complex viscosity (η^*) and the angular frequency (ω) with a gradient close to −1 suggests a regular decrease in viscosity with increasing frequency.

The mechanical strength of the gel was measured using G' and G'' as a function of shear stress at 22 °C and a frequency of 1 rad s^{-1}. Over a large range of shear stress, G' supersedes G'' by ~1 order of magnitude, which clearly indicates a gel phase material.[9] Notably, with a gradual increase in the applied stress, both G' and G'' remained almost invariant and cross each other only at a certain yield stress (1.3 Pa), showing nonlinear properties and indicating mechanical breaking of the gel beyond the yield stress following a phase transition (*gel–sol*). On the other hand, **IGM** is mechanically stable for an applied strain up to 1.2% (Fig. S10, ESI†). Frequency sweep measurements showed G' and G'' to be frequency independent in the frequency region (−0.2–1.5 rad s^{-1}). As $G' > G''$, this suggests that the **IGM** behaves as a gel phase material. The gelation property was also probed by comparative PXRD patterns for **1** and its xerogel. The loss of the peaks due to xerogel established its amorphous nature (**IGM**) (Fig. S11, ESI†).[10] Based on the above results, it is concluded that saponification is the key observable step that induces significant conformational change in **1** by the *in situ* conversion of the ester into carboxylate, thereby increasing the π-interactions by manifolds to create a true phase gel material (**IGM**) (Fig. S14, ESI†).[11]

In summary, through this work the applicability of the saponification process to trigger gelation in a Zn(II) complex has been demonstrated. Gelation is accompanied by substantial conformational changes encompassing gel-phase oriented π-stacking/cation–π interactions. This has been thoroughly demonstrated by various spectral (UV/vis, fluorescence, ^{1}H NMR) and DFT studies, and the true gel phase was also affirmed by rheological investigations. Therefore, through this work a novel methodology based on saponification-triggered gelation for inorganic complexes has been established.

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