Supporting Information for

Mechano-switchable, Luminescent Gels Derived from Salts of a Long-chained, Fatty-acid Gelator

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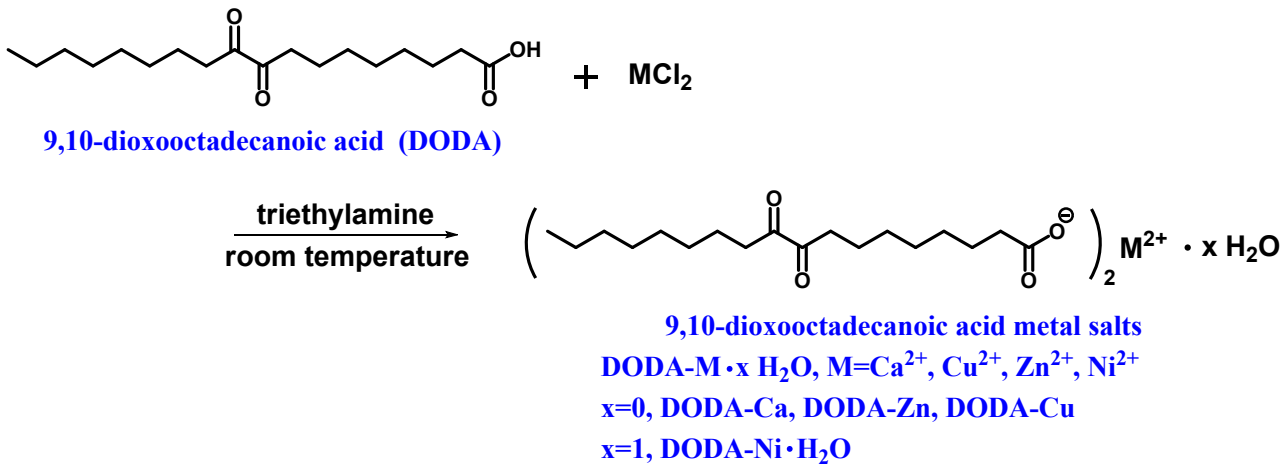
Materials and Instrumentation

Materials.

9,10-Dioxooctadecanoic acid (**DODA**) was prepared according to a published procedure.[1] Triethylamine (Alfa Aesar, 99%), nickel(II) chloride hexahydrate (Alfa Aesar, 98%), cupric chloride (J. T. Baker Chemical), zinc chloride (Fisher Scientific, 98.6%), calcium chloride (Fisher Scientific, anhydrous), methanol (anhydrous, Sigma-Aldrich, 99.8%), ethanol (Sigma-Aldrich, 200 proof, anhydrous, 99.5%), 1-octanol (Sigma Aldrich, >99%), acetonitrile (Fisher Scientific, certified A.C.S), ethyl acetate (Sigma-Aldrich, HPLC, 99.7%), chloroform (Fisher Scientific, 99.6%), carbon tetrachloride (Fisher, HPLC 99.9%), toluene (EMD Chemicals, 99.8%), hexylbenzene (Aldrich, 97%), benzonitrile (Matheson Coleman & Bell Manufacturing Chemists, 98%), nitrobenzene (Sigma, 99%), chlorobenzene (Alfa Aesar, certified A.C.S, 99.5%), distilled water, and decane (Sigma Aldrich, >99%) were used as received.

Syntheses

The metal salts of 9,10-dioxooctadecanoic acid were synthesized from the acid (**DODA**), triethylamine, and a metal salt--nickel(II) chloride hexahydrate, cupric chloride, zinc chloride, or calcium chloride—using the same procedure (Scheme S1). Details for the nickel(II) 9,10-dioxooctadecanoate monohydrate (**DODA-Ni • H_2O**) synthesis are presented below.



Scheme S1. Syntheses of 9,10-dioxooctadecanoic acid metal salts (**DODA-M • xH_2O**).

DODA (303 mg, 0.97 mmol) was dissolved in 3 mL of chloroform. Triethylamine (98 mg, 0.96 mmol) was dissolved in 0.5 mL of chloroform separately and it was added to the **DODA** solution dropwise. The mixture was stirred for 3 h. Nickel(II) chloride hexahydrate (115 mg, 0.48 mmol) was dissolved in 0.5 mL methanol and added dropwise. The mixture was further stirred overnight and the solvent was removed under a stream of nitrogen at room temperature. The residual solid was stirred sequentially in ethyl acetate (5 mL), water (5 mL), and methanol (2 × 5 mL) for 30 min each and then vacuum filtered to yield 206 mg (61 %) of nickel(II) 9,10-dioxooctadecanoate monohydrate (**DODA-Ni • H_2O**).

For **DODA-Ni • H_2O**: 61 % yield of a green solid that did not melt below its decomposition temperature (139 °C, Figure S1). IR (υ_{max}/ cm^{-1}): 2922, 2849 (C-H stretching), 1711 (α-diketone,[2] C=O stretching), 1558 (COONi, C=O asymmetric stretching), and 1408 (COONi, C=O symmetric stretching). Elemental analysis (EA) (%) calculated for $C_{36}H_{64}O_9Ni$: C, 61.81; H, 9.22; N, 0.00. Found: C, 61.93; H, 9.23; N, 0.06.

For **DODA-Ca**: 35 % yield of a yellow solid that did not melt below its decomposition temperature (130 °C, Figure S1). IR (υ_{max}/ cm^{-1}): 2922, 2848 (C-H stretching), 1711 (α-diketone,[2] C=O stretching), 1572 (COOCa, C=O asymmetric stretching), and 1436 (COOCa, C=O symmetric stretching). ^{1}H NMR (DMSO-d_6, 400 MHz) δ (ppm): 2.64-2.68 (t, 4H, -C**H_2**C(=O)C(=O)-C**H_2**-, J = 8 Hz), 2.04-2.08 (t, 2H, C**H_2**-COOH, J = 8 Hz), 1.40-1.46 (m, 6H, -C**H_2**CH_2C(=O)C(=O)CH_2C**H_2**- and -C**H_2**-CH_2-COOH), 1.10-1.30 (m, 16H, C**H_2**-CH_2), 0.82-0.85 (t, 3H, C**H_3**, J = 6 Hz). EA (%) calculated for $C_{36}H_{62}O_8Ca$: C, 65.22; H, 9.43; N, 0.00. Found: C, 65.50; H, 9.07; N, 0.10.

For **DODA-Zn**: 69 % yield of a pale yellow solid that did not melt below its decomposition temperature (134 °C, Figure S1). IR (υ_{max}/ cm^{-1}): 2919, 2848 (C-H stretching), 1711 (α-diketone,[2] C=O stretching), 1544 (COOZn, C=O asymmetric stretching), and 1407 (COOZn, C=O symmetric stretching). ^{1}H NMR (DMSO-d_6, 400 MHz) δ (ppm): 2.65-2.67 (t, 4H, -C**H_2**C(=O)C(=O)-C**H_2**-, J

= 8 Hz), 2.03-2.07 (t, 2H, C**H$_2$**-COOH, J = 8 Hz), 1.40-1.46 (m, 6H, -C**H$_2$**CH$_2$C(=O)C(=O)CH$_2$C**H$_2$**- and -C**H$_2$**-CH$_2$-COOH), 1.10-1.30 (m, 16H, C**H$_2$**-CH$_2$), 0.82-0.85 (t, 3H, C**H$_3$**, J = 6 Hz). EA (%) calculated for $C_{36}H_{62}O_8Zn$: C, 62.82; H, 9.07; N, 0.00. Found: C, 62.73; H, 9.27; N, 0.12.

For **DODA-Cu**: 48 % yield of a blue solid that did not melt blow its decomposition temperature (125 °C, Figure S1). IR (υ_{max}/ cm^{-1}): 2920, 2848 (C-H stretching), 1711 (α-diketone,[2] C=O stretching), 1587 (COOCu, C=O asymmetric stretching), and 1414 (COOCu, C=O symmetric stretching). EA (%) calculated for $C_{36}H_{62}O_8Cu$: C, 62.99; H, 9.10; N, 0.00. Found: C, 62.85; H, 9.34; N, 0.14.

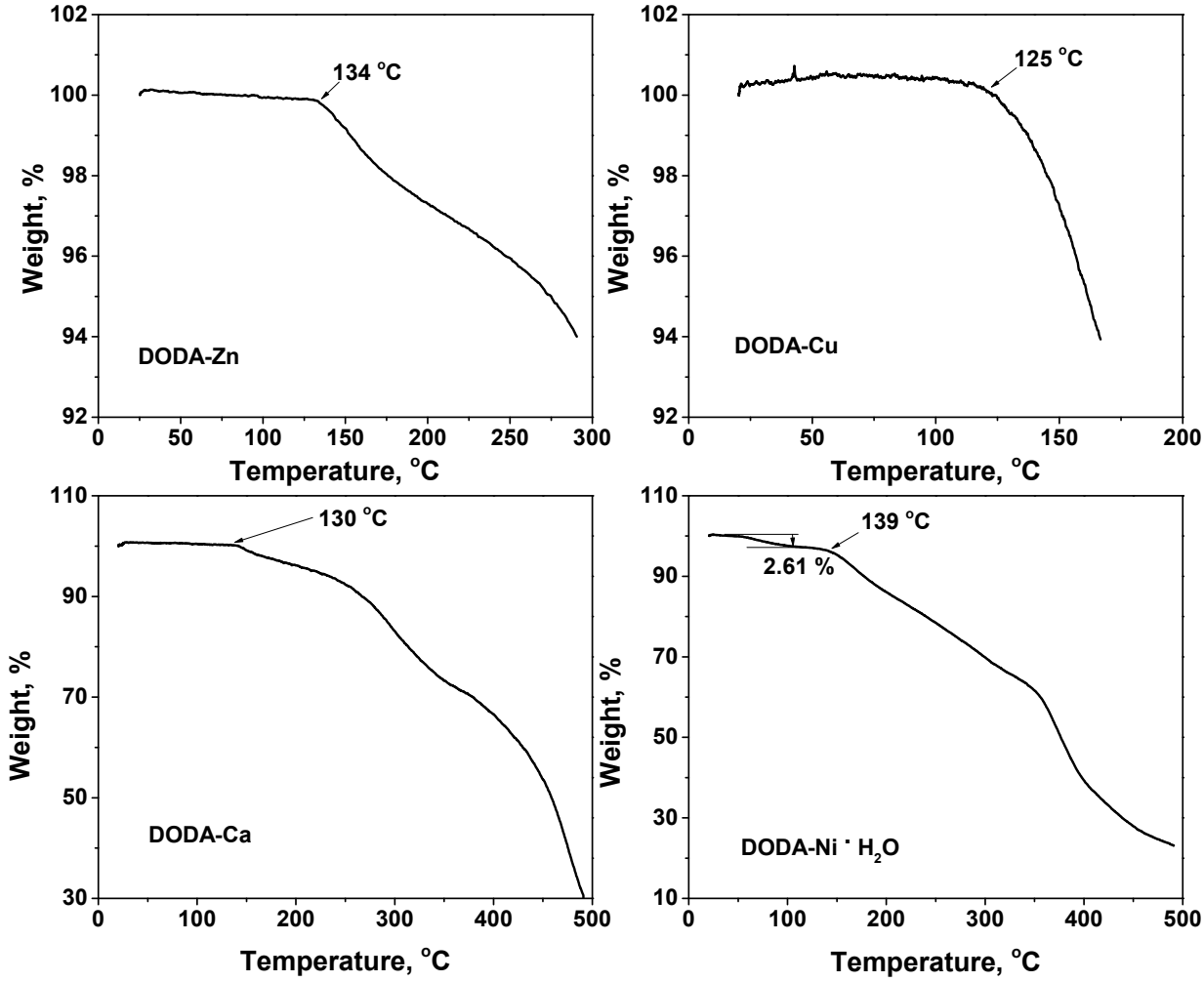


Figure S1. Weight loss as a function of temperature by thermal gravimetric analysis (TGA) for **DODA-M • xH_2O** neat solids.

All of the **DODA** metal salts prepared started to decompose between 125 and 140 °C (Figure S1). Thus, all of the **DODA-M • xH_2O** were heated no higher than 120 °C during gelation studies. There was an additional weight loss for **DODA-Ni • H_2O** at 70-100 °C. This loss is consistent with the presence of a monohydrate (as indicated by the elemental analysis).

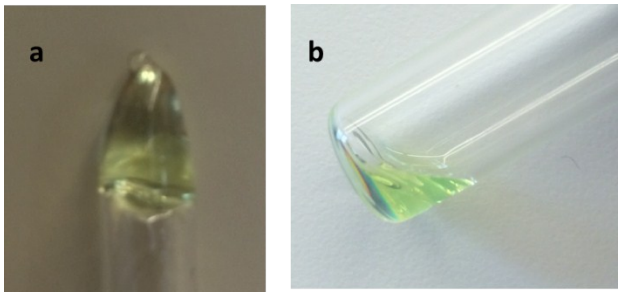


Figure S2. Appearance of a mixture of (a) 5 wt % **DODA-Ni • H_2O** in toluene and (b) 5 wt % anhydrous **DODA-Ni** in dry toluene.

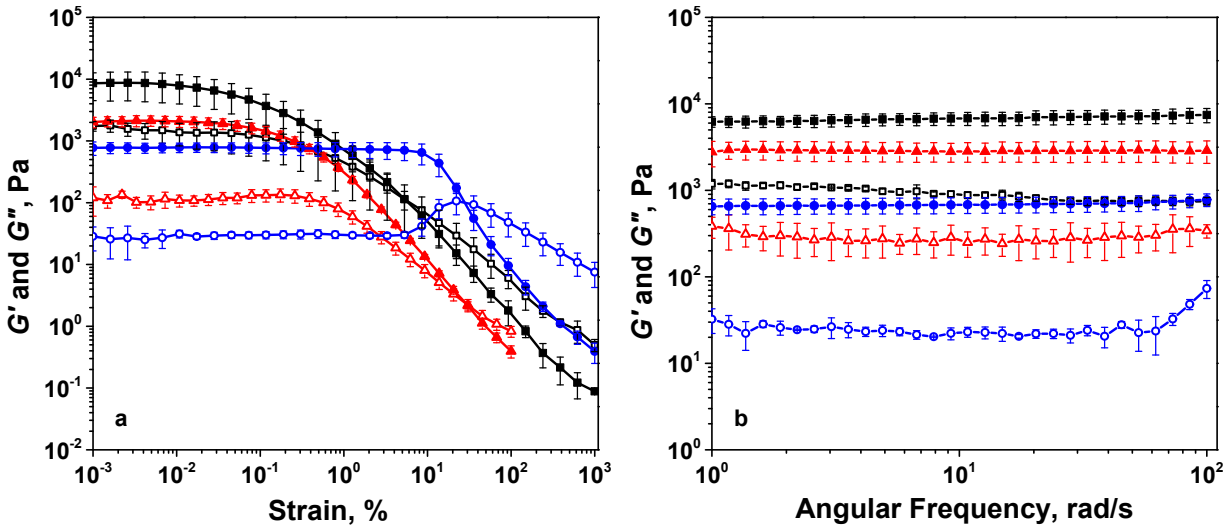


Figure S3. Log-log plots of strain sweeps (a, frequency = 1Hz) and angular frequency sweeps (b, strain = 0.01%) for gels of 5 wt % **DODA** (■,□),[1] **DODA-Cu** (▲,△), and **DODA-Ni • H_2O** (●,○) in benzonitrile. *G′* are closed symbols and *G″* are open symbols.

Table S1. *G′*, *G″*, tan *δ* (at 0.01 % strain), and yield strains (i.e., crossover points) of gels with 5 wt% gelator in benzonitrile.

gel	*G″* (Pa)	*G′* (Pa)	tan *δ* (*G″*/*G′*)	crossover point (%)
DODA[a]	930±160[a]	6800±370[a]	0.14±0.03[a]	5[a]
DODA-Cu	290±40	2900±50	0.10±0.02	25
DODA-Ni • H_2O	30±10	700±30	0.04±0.01	28

[a] From ref 1.

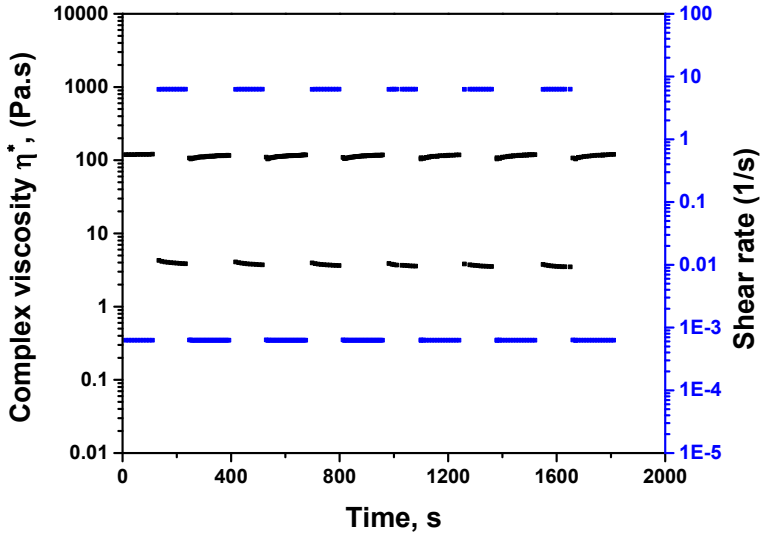


Figure S4. Complex viscosity (η^*) as a function of time and application of different strains to samples in benzonitrile of 5 wt % **DODA-Ni • H_2O** at 20 ºC. Linear viscoelastic region (LVR): γ = 0.01 %, f = 1 Hz; destructive strain region (DS): γ = 100 %, f = 1 Hz. Rotational strain was kept at 0 % for 1 s before changing from DS to LVR conditions. Data points were collected every 1 s after the cessation of destructive strain.

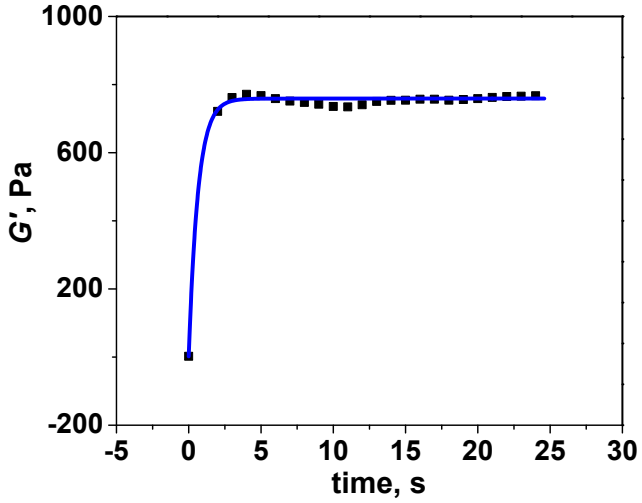


Figure S5. The best fit to a single exponential rise (blue line)[3, 4] for the recovery data of *G′* (dots, data averaged from 6 cycles, starting from the first cycle) for a gel of 5 wt % **DODA-Ni • H_2O** in

benzonitrile at 20 ºC after cessation of destructive strain (DS) and return to the linear viscoelastic (LVR) condition.

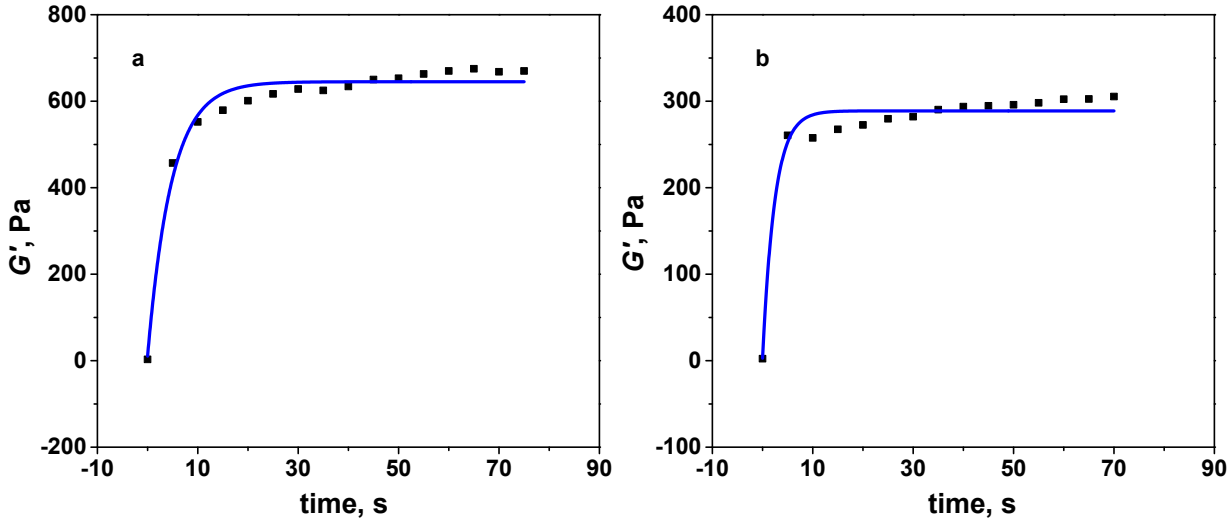


Figure S6. The best fit to a single exponential rise (blue lines)[3, 4] for the recovery data of G' (dots) for a gel of 5 wt % **DODA-Cu** in benzonitrile at 20 ºC after cessation of DS and return to the LVR condition. (a) Data collected from the first cycle. (b) Data averaged from 6 cycles, starting from the second cycle.

Table S2. Thixotropic parameters related to gels of 5 wt % **DODA-Cu** and **DODA-Ni • H_2O** gels in benzonitrile: recovery times (τ), % of thixotropic recovery and loss tangent after different numbers of LVR-DS cycles.

	τ (s)	% of thixotropic recovery [a]	tan δ (G'' /G')
DODA-Ni • H_2O average of all cycles	< 3	~100 %	0.04±0.03
DODA-Cu 1st cycle	< 10	~20 %	0.13±0.03
DODA-Cu average of 6 cycles starting from the 2nd cycle	< 5	~10 %	0.14±0.03

[a] percentage recovery of the G' value taking the initial G' value as 100 %.

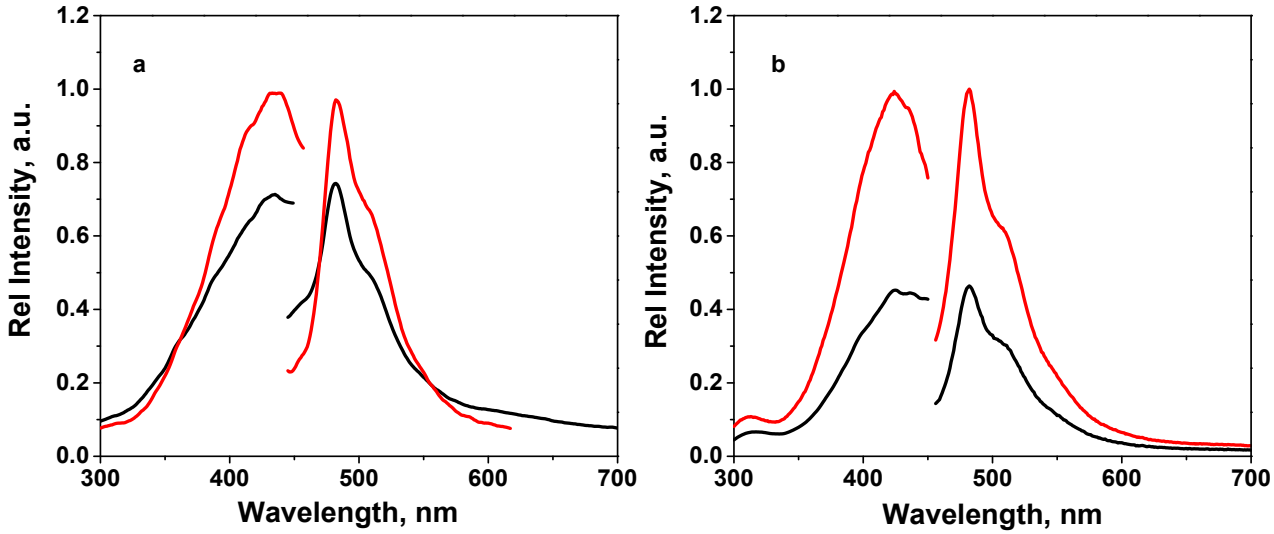


Figure S7. Excitation (λ_{em} 481 nm) and emission spectra (λ_{ex} 425 nm) of (a) a 5 wt % **DODA-Cu** in CCl_4 gel at 25 °C (black) and its sol at 70 °C (red); (b) a 5 wt % **DODA-Ni • H_2O** in 1-octanol gel at 25 °C (red) and its sol at 80 °C (red).

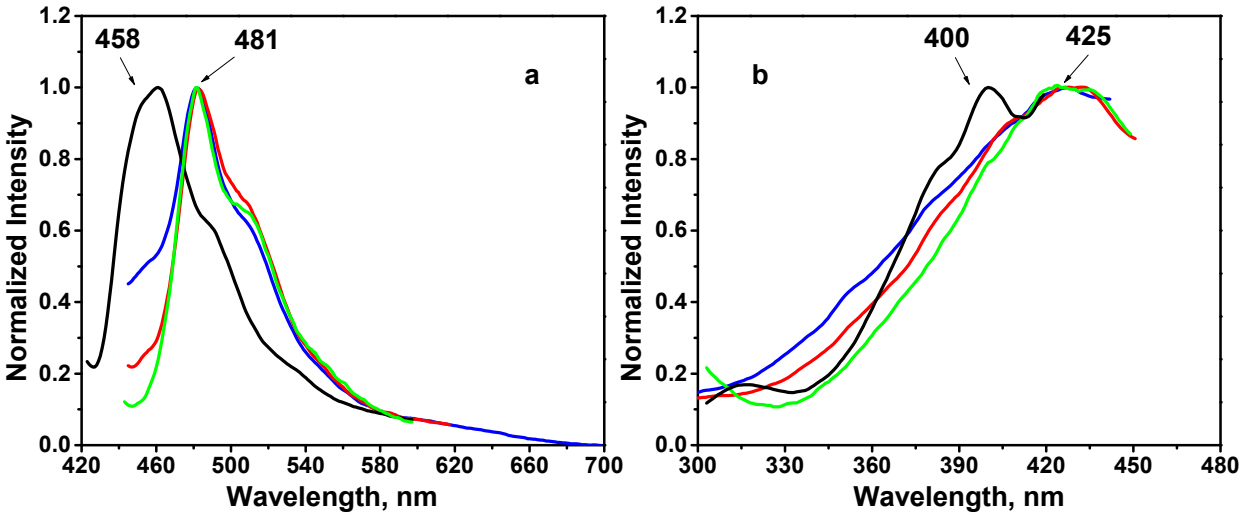


Figure S8. Normalized (a) emission and (b) excitation spectra of a 5 wt% **DODA-Cu** in CCl_4 gel at 25 °C (red, λ_{em} 481 nm, λ_{ex} 425 nm), its sol at 70 °C (blue, λ_{em} 481 nm, λ_{ex} 425 nm), a 5 wt% **DODA** in CCl_4 gel at 25 °C (black, λ_{em} 458 nm, λ_{ex} 400 nm), and its sol at 45 °C (green, λ_{em} 481 nm, λ_{ex} 425 nm).

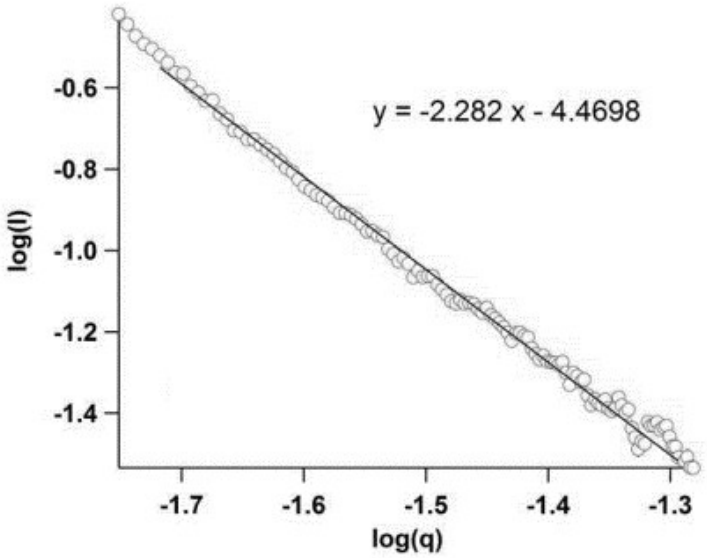


Figure S9. Porod plot of SAXS data in the high *q* region (0.019-0.052 Å^{-1}) for a gel of 5 wt% **DODA-Ni • H_2O** in benzonitrile.

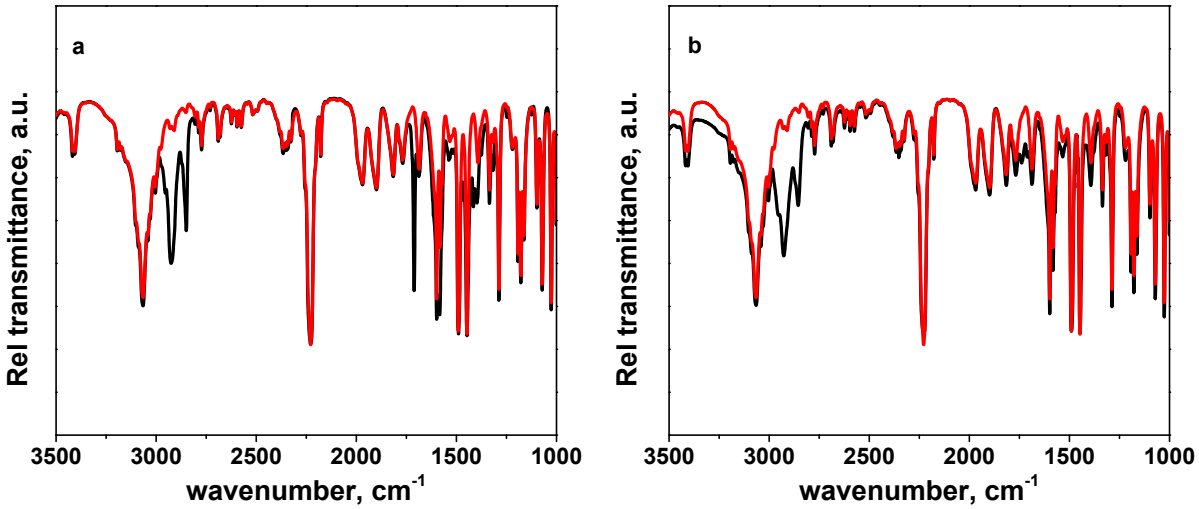


Figure S10. FT-IR spectra of (a) gels of 5 wt % **DODA-Cu** (black) in benzonitrile without empirical subtraction of the benzonitrile peaks and neat benzonitrile (red); (b) gels of 5 wt % **DODA-Ni • H_2O** (black) in benzonitrile without empirical subtraction of the benzonitrile peaks and neat benzonitrile (red).

Table S3. Wavenumbers of symmetrical and asymmetrical stretching bands of carboxylate groups, and the assigned major coordination modes (see main text) from FT-IR spectra of neat **DODA** salts and 5 wt% gels in benzonitrile. .

	υ_{asym} OCO	υ_{sym} OCO	Separation	coordination type
DODA-Ca (neat)	1572 cm^{-1}	1409 cm^{-1}	163 cm^{-1}	bridging

DODA-Zn (neat)	1544 cm^{-1}	1407 cm^{-1}	137 cm^{-1}	chelating
DODA-Cu (neat)	1587 cm^{-1}	1414 cm^{-1}	173 cm^{-1}	bridging
DODA-Cu (gel)	1588 cm^{-1}	1415 cm^{-1}	173 cm^{-1}	bridging
DODA-Ni·H_2O (neat)	1560 cm^{-1}	1410 cm^{-1}	150 cm^{-1}	bridging
DODA-Ni·H_2O (gel)	1562 cm^{-1}	1412 cm^{-1}	150 cm^{-1}	bridging

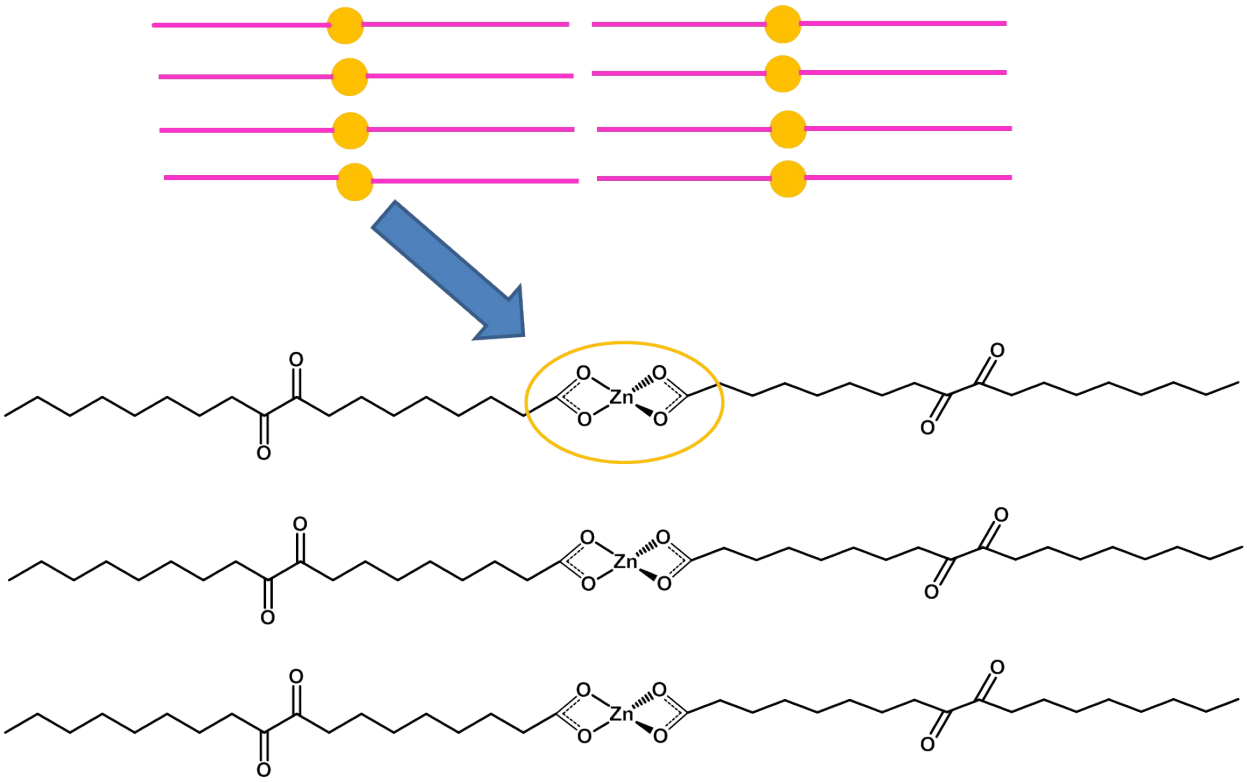


Figure S11. Schematic representation of the proposed molecular packing arrangement for neat **DODA-Zn**.

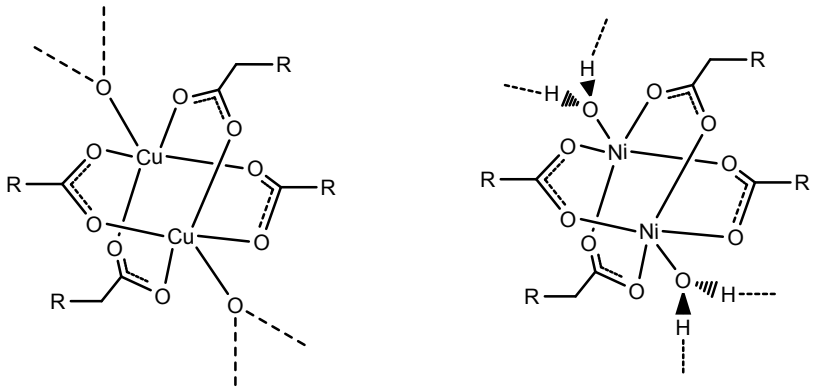


Figure S12. Schematic representation of the proposed dimeric molecular packing arrangement for neat **DODA-Cu** and **DODA-Ni • H_2O**. R group represents a polymethylene chain.

References:

1. M. Zhang and R. G. Weiss, *Chem. Eur. J.*, 2016, **22**, 8262-8272.
2. A. Gómez-Zavaglia and R. Fausto, *J. Mol. Struct.*, 2003, **661–662**, 195-208.
3. H. A. Barnes, *J. Non-Newton. Fluid*, 1997, **70**, 1-33.
4. J. Mewis and N. J. Wagner, *Adv. Colloid Interface Sci.*, 2009, **147-48**, 214-227.