Electronic Supplementary Information (ESI)

Hierarchical aggregation mechanism in heat-set metallosupramolecular gels using a tritopic functional ligand exhibiting temperature-triggered *cis*-to-*trans* molecular conversions

*Minhao Yan[1], Sabareesh K. P. Velu[1], Manuel Maréchal[2], Guy Royal[3], Jose Galvez[1] and Pierre Terech[*1]*

1 Structure et Propriétés d'Architectures Moléculaires UMR5819 (CEA-CNRS-UJF), INAC/SPrAM, CEA Grenoble, 17 rue des Martyrs, 38054-Grenoble-cedex9, France

2 LEPMI UMR 5279 (CNRS-Grenoble INP-Université de Savoie-Université Joseph Fourier), BP 75, 38402 Saint Martin d'Hères, France

3 Université Joseph Fourier Grenoble I, Département de Chimie Moléculaire, UMR CNRS-5250, Institut de Chimie Moléculaire de Grenoble, FR CNRS-2607, BP 53, 38041, Grenoble Cedex 9, France

S1 – DLS: gelation study

For **Ni_2BTC** solution (s = 2, C_{BTC} = 40 mM), the DLS study exhibits correlation functions shifting to larger characteristic times when the temperature is increased to 50°C (Fig. S1).

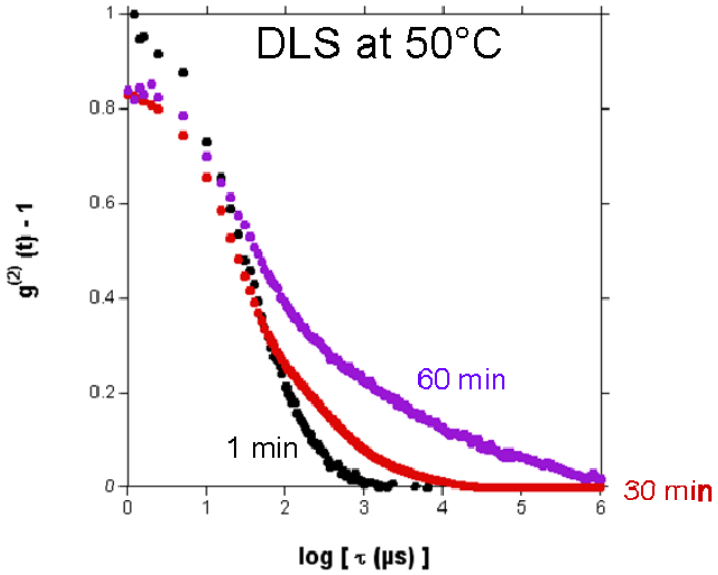

Fig. S1 DLS of the **Ni_2BTC** solution (s = 1.8, C_{BTC} = 40 mM): intensity autocorrelation functions as a function of annealing time at 50°C.

S2 – DLS: Ni_2BTC solutions of different concentrations

The normalized time-averaged intensity-intensity autocorrelation function for different concentrations (10mM, 20mM, 30mM and 40mM) of **Ni_2BTC** solutions (s = 1.8) at scattering angle 90^o for two temperatures is shown in Fig. S2a & S2b. For 10mM concentration, the scattering signal is too weak to detect the correlation curve and notice the characteristic relaxation time shifts to higher times with increase in concentration (20mM to 40mM) at 18^{o}C (Fig. S2a). Heating the **Ni_2BTC** solutions at 50^{o}C improves the scattering signal for all concentrations including 10mM solution and again the characteristic relaxation time shifts to higher time scales with increase in concentration (10mM to 40mM) see Fig. S2b. For 40mM

at 50°C, notice the initial amplitude of correlation curve drops rapidly. This feature corresponds to frozen-in-structures (non-ergodicity) as they undergo gel transition.

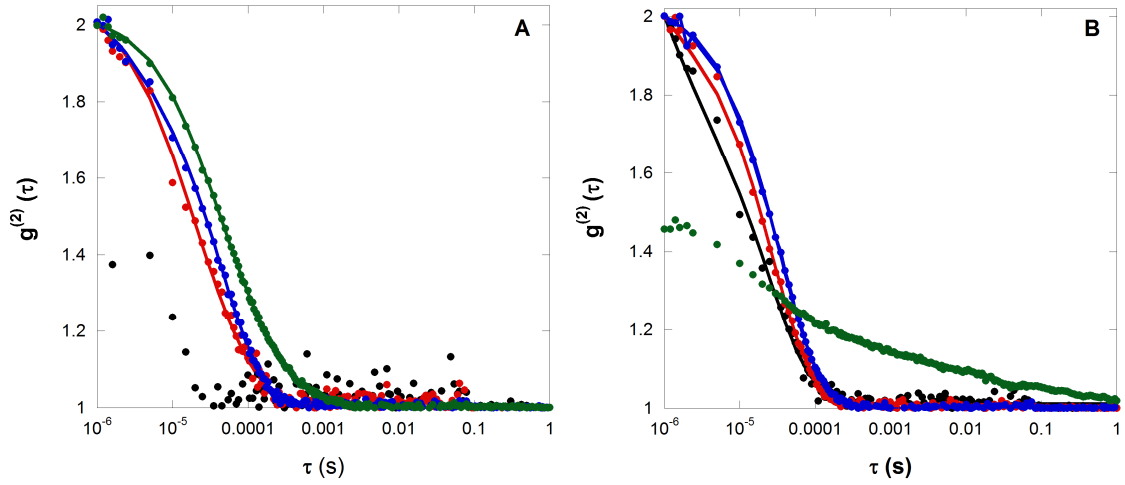

Fig. S2 Normalized intensity-intensity autocorrelation function for 10mM (black), 20mM (red), 30mM (blue) and 40mM (green) concentrations of **Ni_2BTC** solutions (s = 1.8) measured at scattering angle 90° for temperature 18°C (a) and 50°C (b).

S3 – Interaction of aggregates in Ni_2BTC solutions

Interactions are studied by measuring the time-averaged intensity-intensity autocorrelation functions as a function of scattering angles for all concentrations. The auto-correlation functions measured as a function of scattering angles when plotted versus $Q^2\tau$ exhibits complete collapse for all concentrations except for 40mM Ni_2BTC solutions at 50 °C (gel-like system) revealing the scattering species under go simple Brownian motions and they are not affected by any interaction between each species. Fig. S3a and S3b shows the normalized auto-correlation function for 30mM Ni_2BTC solutions (s = 1.8) for different scattering angles (40°, 50°, 70°, 90°, 110° and 130°) versus $Q^2\tau$ for two temperatures.

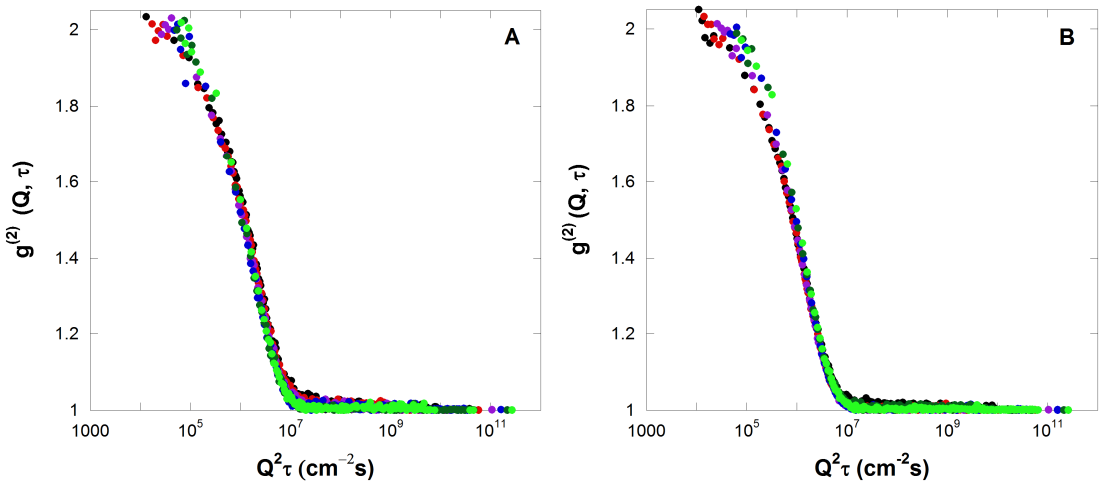

Fig. S3 Normalized intensity-intensity auto-correlation function for 30mM **Ni_2BTC** solutions (s =1.8) measured at various scattering angles plotted as a function of $Q^2\tau$ at temperature 18°C (a) and 50°C (b).