



Mechanical coupling of multivalent receptors in crown-ether-capped Fe_4L_6 tetrahedra



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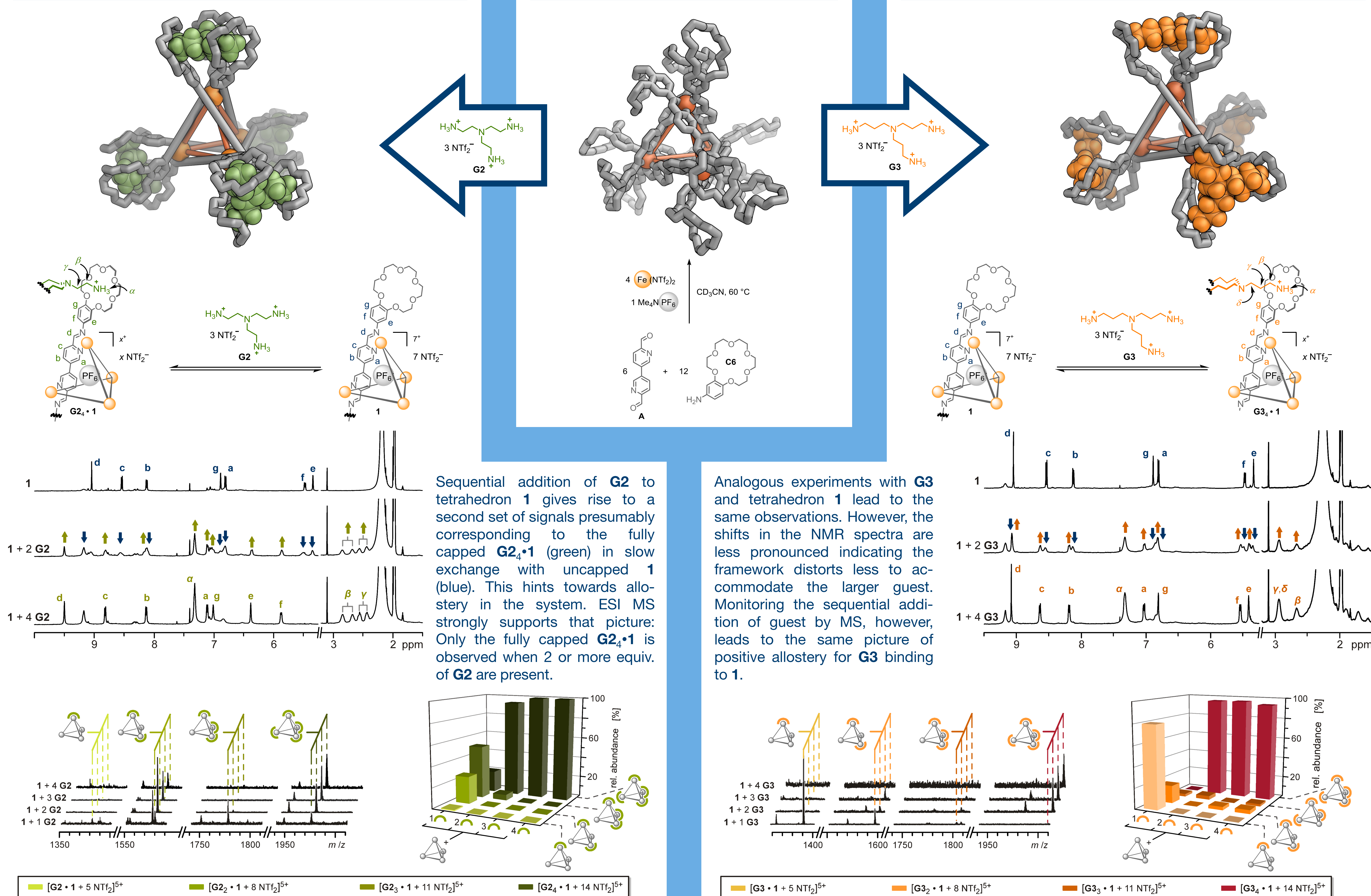
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Flexible receptor can adapt to a smaller tripodal guest

Self-assembly of a multivalent receptor

Flexible receptor can adapt to a larger tripodal guest



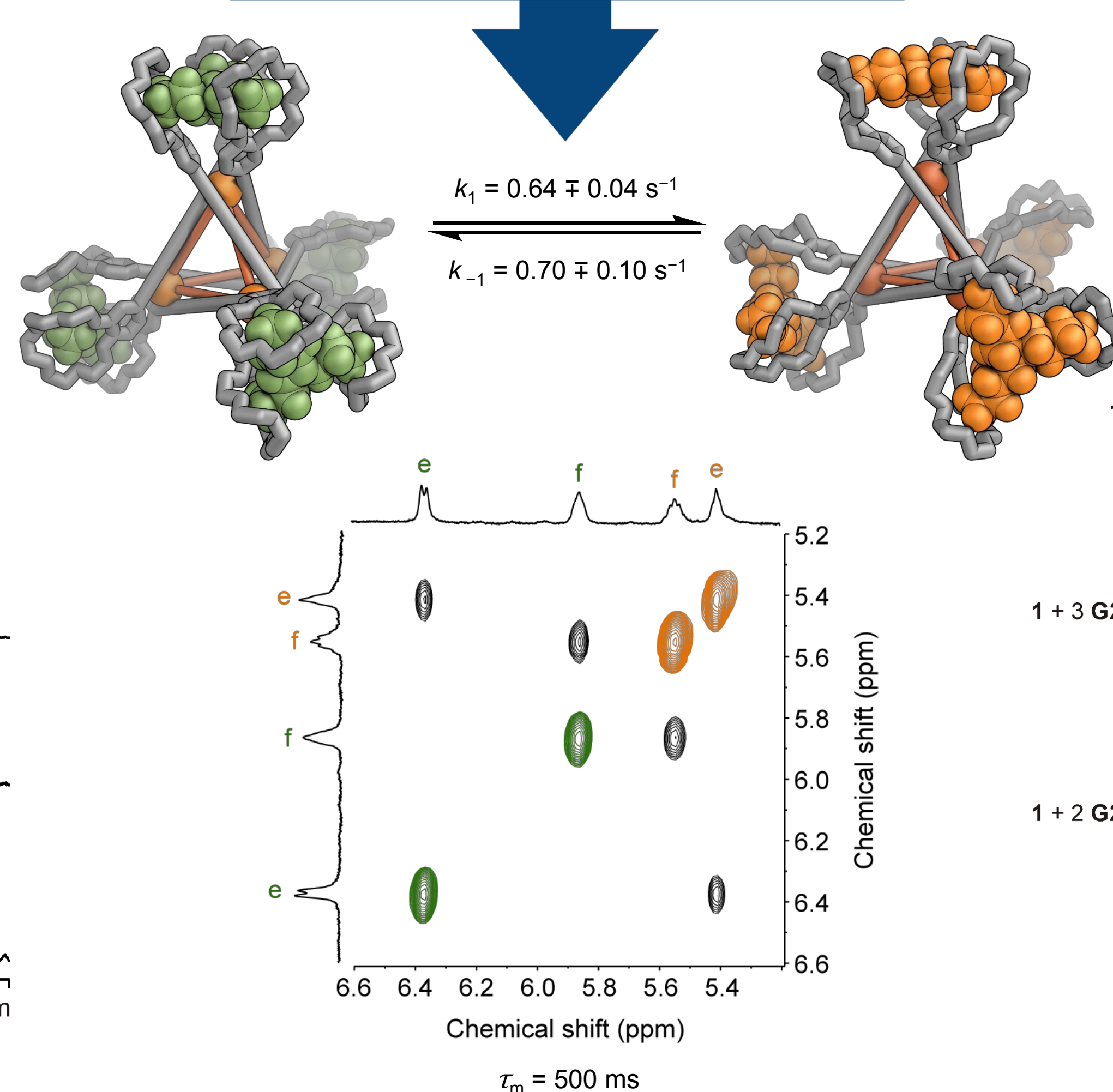
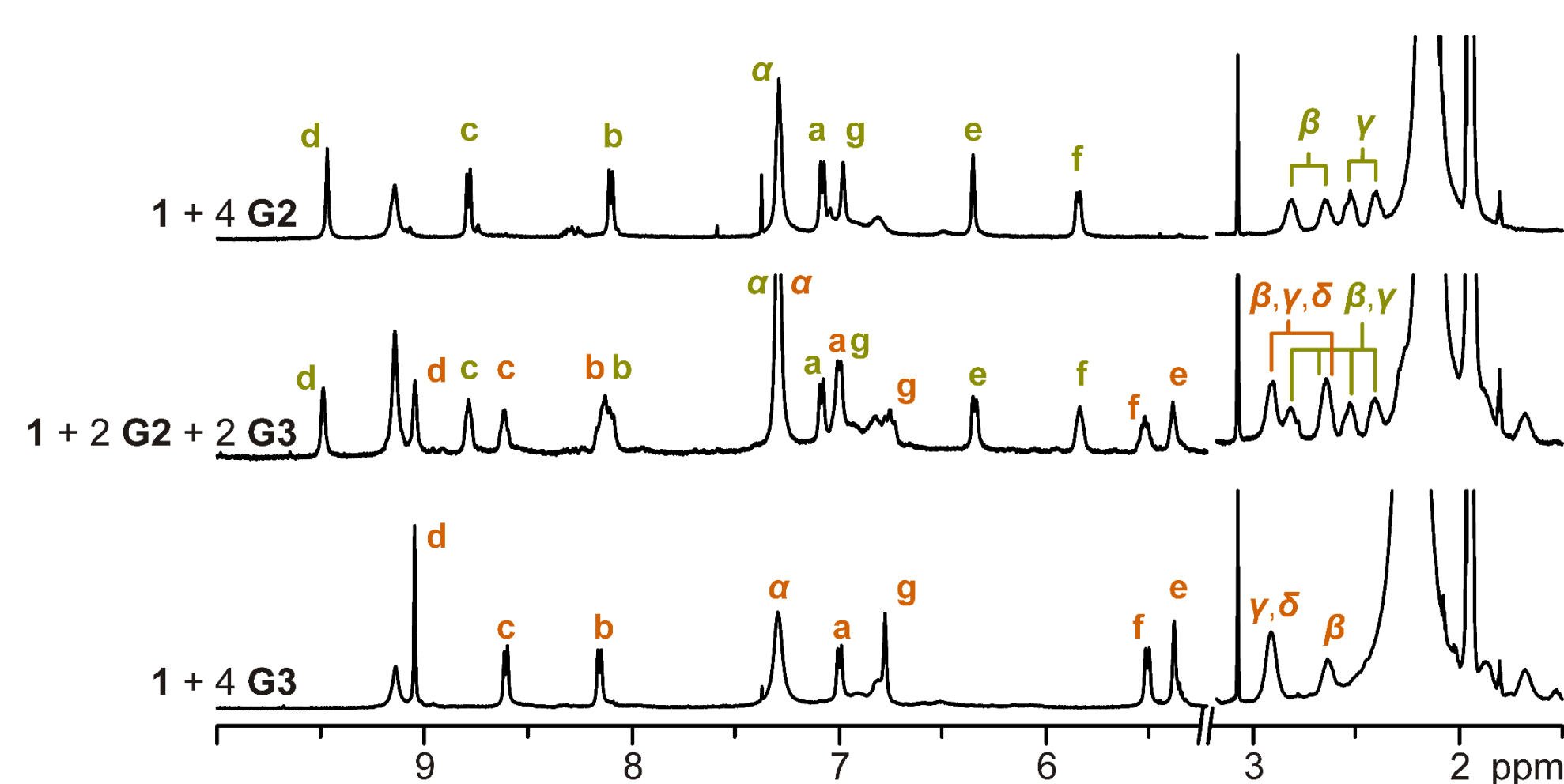
Sequential addition of **G2** to tetrahedron **1** gives rise to a second set of signals presumably corresponding to the fully capped **G2₄·1** (green) in slow exchange with uncapped **1** (blue). This hints towards allostery in the system. ESI MS strongly supports that picture: Only the fully capped **G2₄·1** is observed when 2 or more equiv. of **G2** are present.

Analogous experiments with **G3** and tetrahedron **1** lead to the same observations. However, the shifts in the NMR spectra are less pronounced indicating the framework distorts less to accommodate the larger guest. Monitoring the sequential addition of guest by MS, however, leads to the same picture of positive allostery for **G3** binding to **1**.

Mixing the two systems

Apparent allosteric cooperativity in these systems indicates that the vertices are sterically coupled with each other. That is, binding of one guest facilitates the association of the subsequent guests.

Mixing **G2₄·1** and **G3₄·1** gives rise to an ^1H NMR which is a perfect overlap of the spectra of the two individual components. Both species are in slow exchange with each other. EXSY experiments indicate that the two observed species interconvert within 1.4 s (derived from the first order magnetic exchange rates displayed on the right).



ESI MS of **G2₄·1/G3₄·1** mixtures, however, give rise to statistical distribution of guests **G2** and **G3** bound to the same tetrahedron.

