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Abstract: Vitrimers are 3D "covalent adaptable networks" (CANs) with flow properties thanks to thermally activated associative exchange reactions. The present contribution introduces coordination adaptable networks, or CooANs, that are topologically related to metal-organic frameworks with octahedral Zr_6 clusters as secondary building units in a carboxylic acid-functionalized acrylate-methacrylate copolymer matrix. A series of **Zr-CooAN-x** materials (x = percent of Zr_6 loading relative to maximum capacity) was synthesized with x = 5, 10, 15, 20, 25, 50 and 100. The mechanical and rheological investigations demonstrate vitrimer-like properties for x up to 50, the crosslink migration being ensured by carboxylate ligand exchange, with relaxation becoming slower as the Zr_6 content is increased. The flow activation energy of **Zr-CooAN-10** is 92.9 ± 3.6 kJ mol^{-1}. Rapid (30 min) hot-press reshaping occurs at temperatures in the 50-100 °C range under a 3-ton pressure and does not significantly alter the material properties.

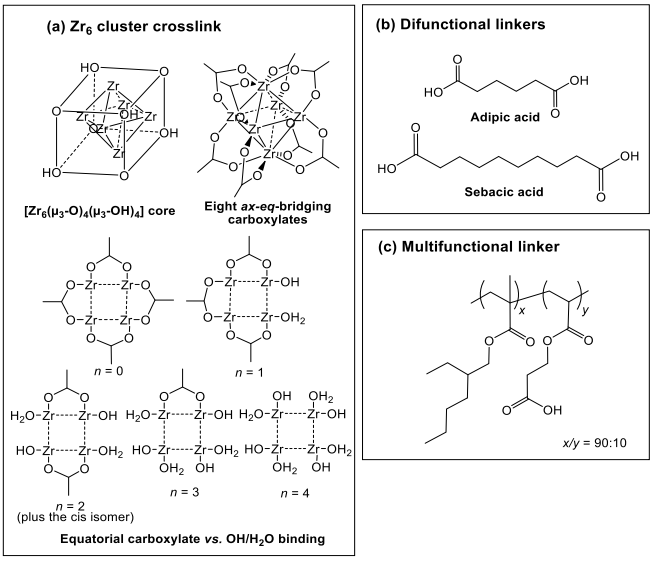
Materials science has experienced a quantum leap with the introduction of covalent adaptable networks (CANs). These are 3D polymers with dynamically exchangeable crosslinks above a certain temperature, hence featuring plasticity, reshaping and recyclability.[1] Thus, they blur the frontier between thermoplastics and thermosets. CANs may be classified in two separate families depending on whether the mechanism of the reversible crosslink exchange reaction is dissociative or associative. The associative CANs, also called vitrimers,[2] have a fixed crosslink density and are characterized by a linear decrease of viscosity when heated above the glass transition temperature, behaving similarly to vitreous silica. Dissociative CANs, on the other hand, are usually characterized by a decrease of connectivity at high temperatures and, like thermoplastics, show a more abrupt transition from solid-like to liquid-like, although certain dissociative CANs were shown to possess virtually indistinguishable stress relaxation and reprocessing properties from those of vitrimers.[3] Various organic reactions have been utilized to develop vitrimers, namely transesterification,[2] transamination,[4] transalkylation,[5] siloxane exchange,[6] disulfide exchange,[7] imine/amine exchange,[8] *etc.*

We have considered the development of hybrid organic-inorganic vitrimers where the associative exchange process is based on ligand exchange in the coordination sphere of a metal-containing crosslink (coordination adaptable networks or CooANs). Reshapable metal-containing 3D materials have previously been described,[9] with crosslinks generated by multiple (>2) valence either in the organic part,[10] or in the metallic ion/cluster,[11] or in both components.[12] Most of these materials function on the basis of coordinative bonds to polymer-linked neutral (2-electron, L-type) donor ligands such as ethers,[12g] imines,[10d] pyridines,[10a, c] (benz)imidazoles[12e, f] and triazoles,[10b, 12c] but a few also involve the exchange of anionic 2-electron ligand (X-type, 1-electron donors in the neutral form), for instance carboxylates,[11, 12d, h] β-diketonates,[10e] catecholates[12a, b] and thiolates,[10f] with excess of the corresponding polymer-anchored XH functions (*i.e.* carboxylic acids, β-diketones, catechols, thiols). Whereas L-type ligands may be exchanged dissociatively, associatively, or by an interchange mechanistic continuum,[13] anionic 2-electron ligand strongly prefer the associative pathway in non-polar media to avoid charge separation, except for the special case of weak bonds susceptible to homolytic cleavage.

In this contribution, we introduce CooANs based on hexanuclear zirconium clusters as crosslinks in a carboxylate-functionalized polymer matrix. Their development was inspired by the well-established metal-organic frameworks (MOFs), also known as porous coordination polymers (PCPs),[14] which are stoichiometric 3D networks assembled by the coordination of metal-based crosslinkers (named "secondary building unit" or SBU in the jargon of this trade) with ligand-functionalized rigid linkers. Because of their stoichiometric composition and linker rigidity, these MOF/PCP materials are characterized by crystallinity, porosity due to large-size channels and absence of dynamic ligand exchange. Therefore, they are not adaptable, even though a few of them reversibly melt or vitrify without decomposition at quite high temperatures on the basis of dissociative processes.[15]

Carboxylates are ubiquitous ligands in MOF/PCP materials. In addition, several molecular metal carboxylates are known to undergo very rapid intramolecular site exchange,[16] while others intermolecularly and rapidly exchange the carboxylate ligands with free carboxylic acids[16g, 17] and even with other metal-bonded carboxylates (scrambling process).[16j, 18] Thus, the combination of carboxylate-based SBUs and flexible linkers holds promise for the development of CooANs. Although very little is known about the carboxylate exchange mechanism in coordination compounds,[17b, t, 19] a dissociative exchange cannot be easily envisaged, not only because of charge separation, which is energetically too costly in a non-polar environment such as a polymer matrix, but also because of the typical bidentate coordination mode of carboxylate ligands, which strengthens the coordinative bond. We have

selected zirconium(IV) because molecular $[Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(O_2CR)_{12}]$ complexes (Scheme 1a), which are models of the SBU in a large variety of MOF/PCPs,[20] were shown to undergo rapid exchange with free carboxylic acids at room temperature in solution (quantitative in less than 10 min).[16g]



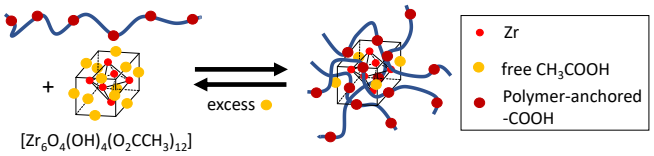
Scheme 1. (a) Structures of the $[Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(O_2CR)_{12\text{-}n}(OH)_n(H_2O)_n]$ clusters (n = 0, 1, 2, 3, 4). (b) Dicarboxylic acid linkers. (c) Polymer linker.

An exploratory approach consisted of the non-stoichiometric (excess carboxylic acid) combination of $[Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(O_2CMe)_{12}]$[16g] and adipic acid (Scheme 1b) in ethanol/water. The reactions produced crystalline precipitates (**1-3**), the composition of which agrees with the incorporation of only four adipates per Zr_6 cluster, according to elemental and TGA analyses (see SI, Table S1, Figures S1-4), irrespective of the adipate/Zr_6 reagents ratio. The same behaviour (four dicarboxylates per Zr_6 unit, irrespective of the diacid/cluster ratio) was also observed when using the longer-chain linker sebacic acid to yield products **4-6** (Scheme 1b). Thus, the reactions involve the exchange of no more than eight of the twelve cluster acetates with the diacid linkers, while a few of the other acetates may be replaced by a combination of OH and H_2O (eq. 1). In this respect, we note that a $[Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(OH)_4(H_2O)_4(O_2CR)_8]$ SBU has also been documented in various MOF/PCPs.[21] Indeed, Zr-based MOFs with only 4 adipate linkers per Zr_6 unit were previously obtained when using the diacid and simple Zr^{4+} salts in a 1:1 ratio.[22] A comparison of the $[Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(O_2CR)_{12}]$ and $[Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(OH)_4(H_2O)_4(O_2CR)_8]$ SBUs suggests a possible compositional variability between acetate and an OH/H_2O combination in the equatorial plane of the Zr_6 octahedron (Scheme 1a), which seems further supported by a ^{13}C NMR investigation of an aqueous solution of Zr^{4+}/CH_3COOH.[23] Evidently, even though flexible, these well-defined linkers favour the assembly of a regular 3D network, though disordered due to compositional variability in the equatorial plane, with exclusion of any excess linkers. It is also relevant to point out that part of the liberated acetic acid remained trapped in the solid product, even after prolonged heating at 120°C under vacuum, as shown by TGA and elemental analyses (Table S1 and Figures S1-2). Single crystals for these new MOF/PCPs could not be obtained and the crystallinities were insufficient to solve the structures from X-ray powder data.

$$[Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(O_2CMe)_{12}] + 4\ HO_2C\text{-}R\text{-}CO_2H + 2n\ H_2O \rightarrow [Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(OH)_{4+n}(H_2O)_{4+n}(O_2CMe)_{4-n}\{O_2C\text{-}R\text{-}CO_2\}_4] + (8+n)\ CH_3CO_2H \quad (1)$$

(R = -$(CH_2)_4$-, -$(CH_2)_8$-)

We then turned to a carboxylic acid-containing disordered polymer (Scheme 1c), made by free radical copolymerization of 2-ethylhexyl methacrylate and 2-carboxyethyl acrylate in a 90:10 ratio[12d] (M_n = 14.4 kmol.g^{-1}; Đ = 2.2), see SEC in Figure S5 and ^1H NMR in Figure S6. The reaction between $[Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(O_2CMe)_{12}]$ and this polymer at various COOH/Zr ratios (Scheme 2) gave a series of different materials (**Zr-CooAN-x**; x = 5, 10, 15, 20, 25, 50, 100), where x is the theoretical molar percent of coordinated polymer carboxylates on the basis of an 8:1 carboxylate/cluster stoichiometry. All products with x up to 50 were recovered from the mould as transparent flexible films, whereas **Zr-CooAN-100** is macroscopically hollow and brittle (Figure S7). The isolated materials are thermally stable, starting to decompose only above 220°C (see TGA in Figure S8). The increasing amount of Zr in the structure is revealed by the IR absorption peak of the coordinated carboxylates at 1593 cm^{-1}, which is sufficiently distinct from the stronger carbonyl vibration of the polymer matrix ester functions (Figure S9). Though the intimate structural nature of the inorganic crosslinks cannot be established from spectroscopic data, the stoichiometry of the reaction with adipic and sebacic acid (eq. 1) suggests a maximum of 8 polymer-bound carboxylates bonded to each Zr_6 unit and a variability of acetate and OH/H_2O ligands binding in the equatorial plane (Scheme 1a). Note, however, that binding to more than eight polymer-linked carboxylates and variable stereochemical ligand arrangements[16g, 24] are possible in a carboxylate-rich environment.



Scheme 2. Schematic representation of the **Zr-CooAN-x** synthesis and of its reverse dissolution in an acetic acid-rich toluene solution.

Table 1. Swelling ratios and insoluble fractions for the **Zr-CooAN-x** materials.

	THF (r.t.)		Toluene (55°C)	
	S.R.[a,b]	I.F.[b,c]	S.R.[a,b]	I.F.[b,c]
Zr-CooAN-5	15±3	0.67±0.05	[d]	[d]
Zr-CooAN-10	12.7±0.4	0.73±0.02	10.1±2.7	0.78±0.11
Zr-CooAN-15	11.8±0.7	0.74±0.04	10.8±2.8	0.85±0.09
Zr-CooAN-20	11.0±1.3	0.78±0.02	10.5±3.4	0.81±0.07
Zr-CooAN-25	8.7±0.9	0.89±0.04	10.8±1.5	0.81±0.06
Zr-CooAN-50	6.4±1.7	0.93±0.02	8.1±0.8	0.93±0.04

Zr-CooAN-100	4.9±1.2	0.98±0.02	5.2±0.6	0.96±0.01

[a] Swelling ratio (weight ratio of swollen and dry sample). [b] The standard deviation on the values is based on four independent experiments. [c] Insoluble fraction (fraction of dried residue after extraction). [d] The results were too erratic.

The swelling ratios and insoluble fractions were determined after treatment/extraction in THF at room temperature and in toluene at 55°C (see Table 1). Both THF and toluene are very good solvents for the polymer matrix. Under both conditions, the swelling ratio decreases and the insoluble fraction increases as the Zr amount is increased, demonstrating the network nature of the materials. It is also notable that the values of both parameters are quite similar for the two different types of treatment and that the fully Zr-loaded **Zr-CooAN-100** sample features essentially zero extractible fraction. The materials could be readily dissolved, however, by reverting the synthesis reaction in toluene solutions containing excess acetic acid (Scheme 2). Experiments carried out with the **Zr-CooAN-10** material showed an increase of the time required for complete dissolution, under identical conditions (weight of the polymer, volume of the solution, shape of the reaction vessel, temperature and rate of stirring), as the acetic acid concentration was decreased while always remaining in large excess (Table S2). This is strong evidence in favour of a first-order dependence in acetic acid for the carboxylate exchange rate, in line with an associative ligand exchange mechanism.

The thermally activated flow was evidenced by rheological analyses. At the relatively low temperature of 100 °C, no modulus plateau was observed in a stress-relaxation plot for **Zr-CooAN-x** with x up to 20 (Figure S10), demonstrating very fast relaxation compared to other CANs.[25] The time required to reach complete relaxation increased with the material Zr content (*i.e.* crosslink density). The non-normalized relaxation curves show that the Zr content also impacts the storage modulus initial value. Frequency sweep measurements were also performed at 160 °C for all samples (Figure 1). The material relaxation is characterized by a crossing of the storage and loss modulus, which is visible only for **Zr-CooAN-5** and **Zr-CooAN-10** under these temperature and frequency range conditions. Higher temperatures/lower frequencies allowed the G'/G'' crossing to be observed for all materials, for instance at 180 °C for **Zr-CooAN-15** (Figure S11). These experiments confirm that relaxation is slower, as expected, as the Zr content increases.

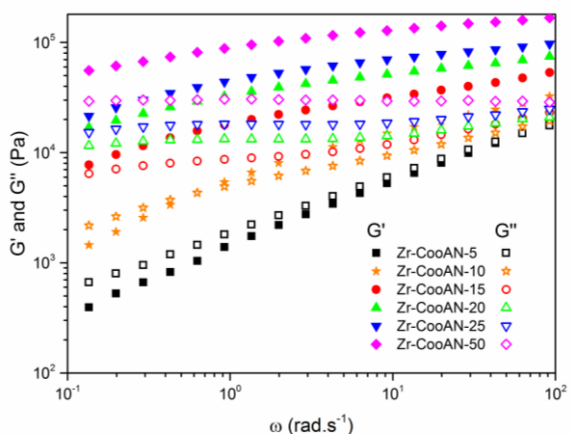


Figure 1. G' (close symbols) and G" (open symbols) measured by frequency sweep on the **Zr-CooAN-x** samples from 10^{2} to 10^{-1} rad s^{-1} at 160 °C.

The frequency sweep measurements on **Zr-CooAN-10** in the 40-160 °C temperature range were used to plot a master curve for the 100 °C reference temperature (Figure 2). The G'/G" crossing at high frequencies signals the end of the glass transition, whereas the sample is stabilized (G' > G'') in the 10^{2}-10^{-1} rad s^{-1} frequency range and relaxation (G" > G') occurs at lower $\omega^{*}a_T$ values. A clear rubbery plateau is not observed because the glass transition and flowing phenomena are thermally close. In order to observe a rubbery plateau, either a lower T_g polymer matrix or a less rapidly exchanging crosslink would be necessary. These observations are consistent with thermally stimulated and rapid carboxylate exchange.

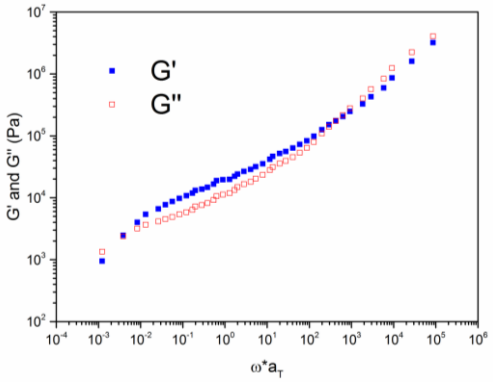


Figure 2. Master curve of the Zr-CooAN-10 sample referenced at 100 °C with G' and G" measured from 40 °C to 160 °C for frequency going from 10^{2} to 10^{-1} rad s^{-1}.

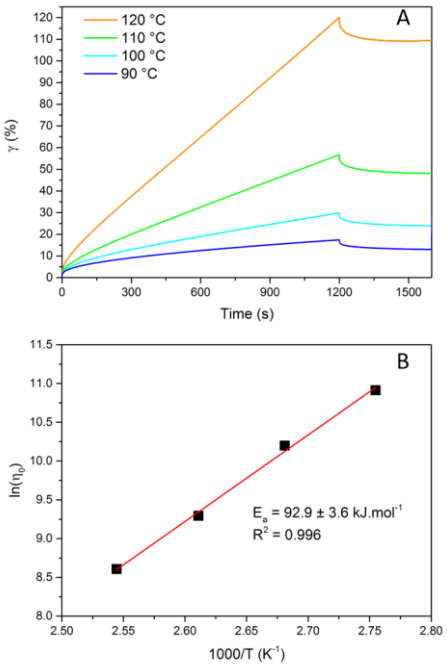


Figure 3. A) Creep and recovery curves of **Zr-CooAN-10** for an applied stress of 500 Pa for 1200 s. B) Arrhenius plot of viscosity determined from the compliance linear region.

Finally, creep and recovery experiments were performed on **Zr-CooAN-10** from 90 to 130 °C (Figure 3A). The initial elastic deformation was recovered when the stress was set back to zero at 1200 s. The compliance ($J_{(t)} = \gamma_{(t)}/\sigma$) from the linear region is inversely proportional to the viscosity ($J_{(t)} = t/\eta_0 + J_0$, where J_0 is the steady-state linear recoverable compliance).[26] The Arrhenius plot of the viscosity (Figure 3B) displayed a vitrimer-like behaviour with a flow activation energy of 92.9 ± 3.6 kJ mol^{-1}.

All **Zr-CooAN-x** with x up to 50 materials can be reprocessed under a 3-ton pressure for 30 min without any visual material degradation (see Figure 4 and Figure S12), the temperature required to produce visually uniform reshaped films being 50 °C for x = 5, 10 and 15, 75 °C for x = 20 and 25, and 100 °C for x = 50. The **Zr-CooAN-100** product could not be reprocessed, even at 150°C in the hot press. Together with the indication that the carboxylate exchange is very rapid (absence of a rubbery plateau for the low-x **Zr-CooAN-x** materials), this is further indication in favour of an associative exchange reaction and also in favour of the carboxylate/Zr_6 8:1 stoichiometry, because the **Zr-CooAN-100** material would have essentially no residual carboxylic acid functions available for the associative exchange. It is necessary to point out, however, that the materials may contain a certain amount of free acetic acid produced by the synthesis, even though they were cured at 120°C under vacuum. Thus, the crosslink migration, though mechanistically associative, may also be mediated by exchange with the free acid and thus become, at least in part, topologically dissociative.[1c]

Figure 4. Images of the pristine and reprocessed **Zr-CooAN-10** material. Equivalent images for all **Zr-CooAN-x** products are available in Figure S12.

The **Zr-CooAN-10** reshaped materials were evaluated by DSC, TGA, IR, DMA and frequency sweep measurements (Table 2). The IR spectrum (Figure S13), TGA plots (Figure S14) and the DSC thermograms (Figure S15) were essentially identical to those of the initial sample, showing that the reshaping process did not affect the material composition, network integrity or glass transition temperature. Finally, the dynamic mechanical analysis (Figure 5) confirmed the negligible effect of reprocessing on the properties (thermal trend, storage moduli, T_α, etc.). It can be noticed that, as seen on the master curve (Figure 2), no clear rubbery plateau was observed as the material directly starts to flow after the glass transition. Frequency sweep experiments performed at 160 °C (Figure 6) demonstrated that the flowing capacity of the reshaped material is essentially the same as that of the pristine sample, with only a slight decrease of the G' and G" values and a slight increase of the flowing frequency (G'/G" crossing at 0.63 and 0.68 rad s^{-1} for the initial and reshaped materials respectively).

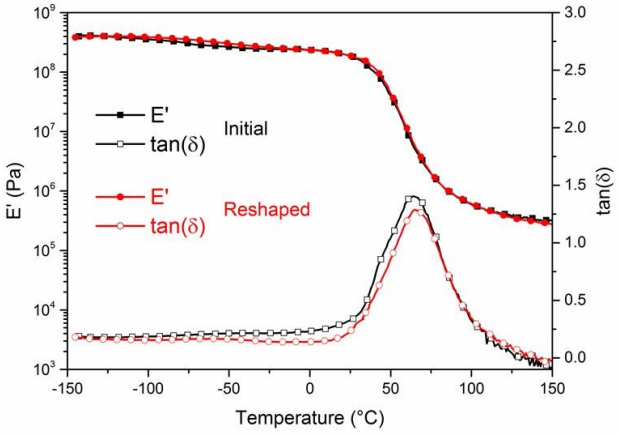


Figure 5. DMA of **Zr-CooAN-10** before and after one reshaping cycle.

Table 2. Overview of the **Zr-CooAN-10** physical properties of before and after reshaping.

	$T_d^{5\,\%}$ (°C)	T_g (°C)	T_α (°C)	$E'_{0\,°C}$ (GPa)	$E'_{125\,°C}$ (MPa)
Initial	281	45	41	0.24	0.40
Reshaped	279	44	39	0.24	0.35

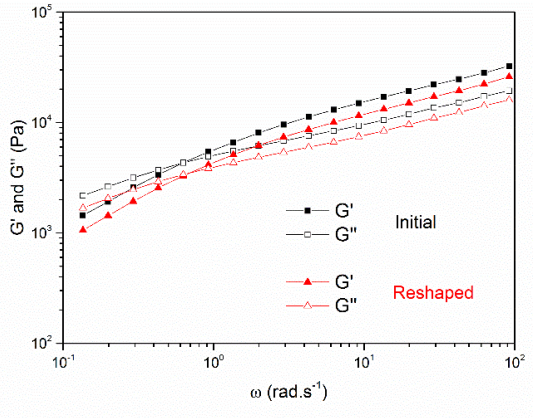


Figure 6. G' (close symbols) and G" (open symbols) measured by frequency sweep at 160 °C on the initial Zr-CooAN-10 sample (black square) and after one reshaping cycle (red triangle).

In conclusion, adaptable polymeric networks crosslinked by the inorganic $Zr_6(\mu\text{-}O)_4(\mu\text{-}OH)_4$ core have been prepared with various crosslinking densities. It is relevant to point out that other polymer networks with $Zr_6(\mu\text{-}O)_4(\mu\text{-}OH)_4$ crosslinks, based on poly(methyl methacrylate) and polystyrene, have previously been generated by radical copolymerization of methyl methacrylate or styrene, respectively, with $[Zr_6(\mu\text{-}O)_4(\mu\text{-}OH)_4(O_2CC(Me)=CH_2)_{12}]$. However, the absence of free acid functions in those networks negates their possible reshaping.[27]

Note also that the same polymer used in the present work was previously shown[12d] to produce self-healing networks upon addition of $[Cu_2(O_2CMe)_4]$, though those materials fully dissolved when immersed into THF.

The **CooAN-Zr-x** materials allow facile low-temperature reshaping without significant impact on properties. The low reprocessing temperature seems related to the fast rate of carboxylate exchange. However, the intimate mechanism of the associative exchange is still unclear. Combining ligand and polymer engineering would be instrumental to better understand and tune the properties of this new class of materials. Work in this direction, as well as the development of CooANs based on other inorganic crosslinks, is ongoing in our laboratories.

Acknowledgements

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Keywords: Vitrimer • Zirconium • Coordination adaptable network • Rheology • Carboxylate exchange

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Entry for the Table of Contents

Coordination adaptable networks (CooANs) are reshapable materials based on the dynamic and degenerate exchange of coordinative bonds. The materials described here, built by ligand exchange from $[Zr_6O_4(OH)_4(O_2CMe)_{12}]$ and a carboxylic acid-containing polymer matrix, which yields $[Zr_6O_4(OH)_4]$-based crosslinks, display vitrimer-like properties.

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