

Photoactive hexanuclear molybdenum nanoclusters embedded in molecular organogels

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ABSTRACT

Hexanuclear molybdenum clusters are attractive species due to their outstanding photonic properties, and in the past they have been attached to a variety of supports such as organic polymers and inorganic nanoparticles, as described in the recent literature. Here, a cluster of formula $\text{TBA}_2[\text{Mo}_6\text{I}_8\text{Ac}_6]$ (TBA = tetrabutylammonium, Ac = acetate) has been supported on molecular organogels for the first time, resulting in a new soft materials with remarkable photoactivity. Electron and confocal microscopic analyses showed the alignment of the nanoclusters to 1D self-assembled fibres formed by the organic gelator, and emission spectroscopy corroborated the interaction of the emissive clusters with such fibrillary structures. The new hybrid system is a deep-red emissive material (phosphorescence maximum at ca. 680 nm), with chromatic coordinates $x=0.725$, $y=0.274$, capable of generating efficiently singlet oxygen ($^1\text{O}_2$) upon illumination with white light, as demonstrated by the photo-oxygenation of 9,10-dimethylanthracene and 1,5-dihydroxynaphthalene. The organogels can be made in dichloromethane and toluene, and in both solvents display phosphorescence emission and photocatalytic properties.

Hexanuclear molybdenum anionic cluster units with formula $[\text{Mo}_6\text{L}^i_8\text{L}^a_6]^{2-}$ (L^i and L^a are inner and apical ligands respectively) have attracted much attention due to their notable emissive properties (in particular, the iodides, $\text{L}^i = \text{I}$). The synthesis and characterization of a vast collection of such complexes has been described.¹⁻¹⁵ They display phosphorescence in the red and near infrared regions (580-900 nm), when excited with blue light. Apart from the emissive properties, these clusters have a notable capacity to generate singlet oxygen ($^1\text{O}_2$) upon illumination. Hence, the research on these systems has boosted in recent years, providing the numerous applications of $^1\text{O}_2$ in photocatalysis¹⁶ and photodynamic therapy (PDT).¹⁷

A number of metallic clusters have been encapsulated in solid supports, leading to photoactive materials. For instance, they have been entrapped in poly (4-vinylpyridine),^{2,18} poly (1-trimethylsilyl-1-propyne),¹⁹ polyurethane,^{12,20} silicone,^{21,22} amorphous carbon,²³ polymethylmethacrylate,²⁴⁻²⁷ poly(D,L-lactide-co-glycolide),²⁸ polymeric hydrogel nanoparticles²⁹ polystyrene,³⁰⁻³⁵ SiO_2 ,^{8,36-40} and ZnO .^{8,41} Some of these materials have proved useful for technological applications such as solid state emission,^{8,25,41} oxygen sensing,^{19,20} time-gated bioimaging,³⁹ photochemical oxygenations^{2,31,33,34,37} and photodynamic therapy (both anticancer^{28,38,40,42} and antibacterial^{31,34}).

Despite the large number of materials mentioned above, no usage of a molecular organogel as support for any $[\text{Mo}_6\text{L}^i_8\text{L}^a_6]^{2-}$ cluster has been reported. Organogels are soft materials formed by low-molecular weight species forming a self-assembled fibrillary network (SAFiN) able to immobilize bulk solvent, yielding a solid-like appearance.⁴³⁻⁴⁵ Here we describe a new hybrid material comprised by a hexanuclear molybdenum cluster immobilized on an organogel. The new material displays deep-red emission and is able to act as a photocatalyst for oxygenation reactions. In this study we have selected $\text{TBA}_2[\text{Mo}_6\text{I}_8\text{Ac}_6]$ (**1** in Figure 1; Ac is acetate and TBA is

tetrabutylammonium) as a photoactive cluster with well-proven photoactivity.^{31,34} Molecule **2** (Figure 1) was selected as organogelator because it forms efficiently transparent gels in dichloromethane and toluene.

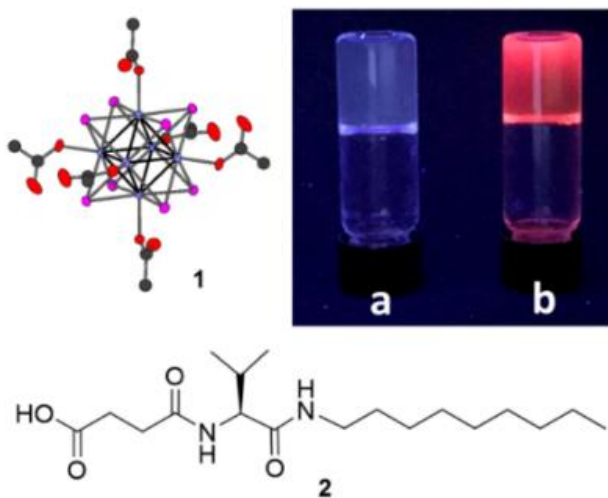


Figure 1. Structures of cluster **1** and molecular organogelator **2**. Picture showing a gel made with **2**, under UV light (a: undoped gel; b: doped with **1**). For both gels $[2] = 14.6 \text{ mM}$ (5 mg/mL) and for b $[1] = 0.25 \text{ mM}$ (0.5 mg/mL).

Gels were prepared by dissolving **1** and **2** at the appropriate concentrations in hot solvent (dichloromethane or toluene) and allowing to cool down to room temperature. After a few minutes, the formation of the gels is evident from the fact that the solvent does not flow after inversion of the recipient (see picture in Figure 1). The gels thus formed are translucent, and upon illumination with UV light of 365 nm display a reddish emission, corresponding to the phosphorescence of **1**. Similar red emission has been reported for hexanuclear molybdenum clusters embedded in polymeric matrices.^{20,25} In the present work we focus on dichloromethane as solvent since gels in this solvent are easier to prepare (lower heating temperature than toluene). Other solvents are currently under study.

The stability of the gels was tested by means of UV-vis absorption measurements at 800 nm. At this wavelength, the transmitted light is scattered in the gel samples (at room temperature), but not when the system is completely fluid (higher temperatures). Using this property, in previous works we were able to determine gelation temperatures (T_g) of gels doped with guest dyes⁴⁶ and nanoparticles.^{47,48} In the case now described a series of variable-temperature absorption measurements afforded a T_g of 32.1 °C, for undoped gel of **2**, and a T_g of 30.3 °C for the hybrid comprised by **1+2** (Figure S1, Supporting Information). This small difference indicates that the stability of the gel is not influenced by the presence of the dopant cluster.

Transmission Electron Microscopy (TEM) analysis of the gels revealed a fibrous structure of self-assembled **2**, similar to analogous materials described so far. Noticeably, the fibres of **1** presented black dots (see Figures 2a,b) corresponding to the incorporated molybdenum clusters (aggregates). Similar associations have been found in hybrid materials formed by SAFINs and CdSe/ZnS quantum dots.^{47,48} The samples were also examined by means of scanning transmission electron microscopy (STEM), and in this case, a higher contrast was found between the supramolecular structures (in grey colour in Figure 2c,d) and the metal cluster aggregates (white dots). The chemical identity of the white spots was confirmed by means of Energy Dispersive X-ray Spectroscopy (EDS) since it showed unequivocally the presence of molybdenum and iodine atoms in the white structures but not in the grey ones. The alignment of the molybdenum clusters in 1D supramolecular scaffolds such as those depicted in Figure 2 has not been reported to date (additional pictures can be seen in the Supporting Information: Figures S4 – S7).

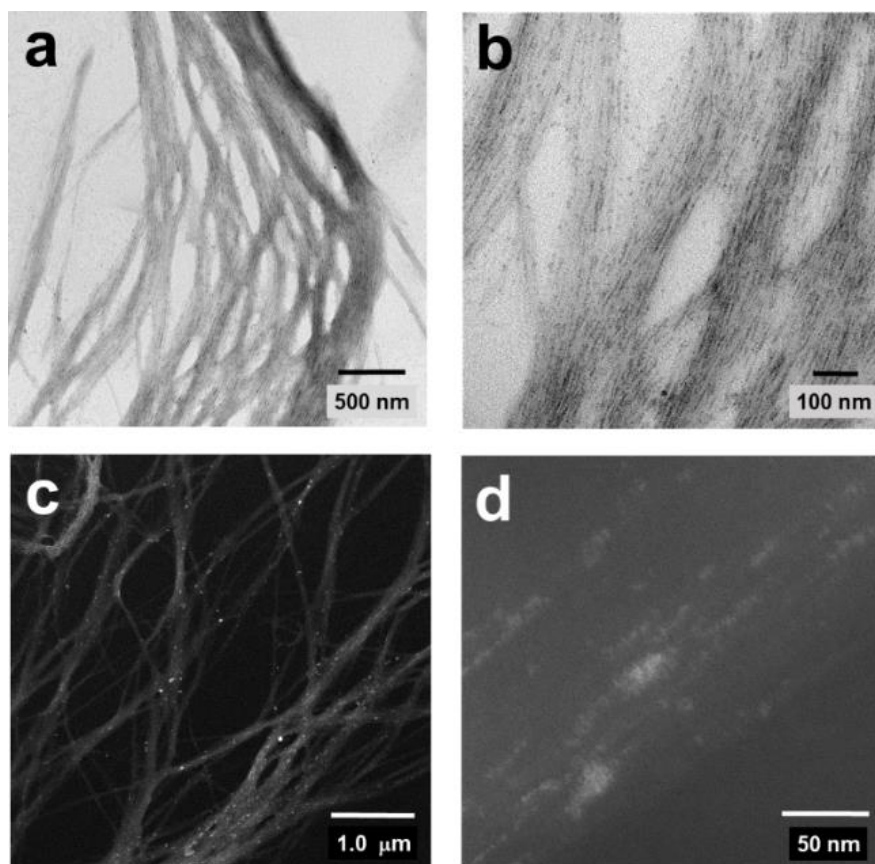


Figure 2. TEM pictures of molecular gels of **2** embedding nanoclusters of **1**. a,b show TEM images of the gels and c,d show STEM images. Conditions: $[2] = 14.6 \text{ mM}$ (5 mg/mL), $[1] = 0.25 \text{ mM}$ (0.5 mg/mL).

The new hybrid materials were also studied by means of confocal laser scanning microscopy (CLSM). This technique has been used by us in the past to study the process of energy transfer in orthogonally assembled fibrillary networks.⁴⁹ In the present case, the dichloromethane gel was examined under the microscope, and a series of long red emitting fibres (several microns length) were observed, when excitation was set to 488 nm (see Figure 3). In order to confirm that this emission was the phosphorescence of the cluster **1** and not an instrumental artifact, the emission spectrum of the fibres was recorded with the confocal microscope. As it can be seen in Figure 4, the maximum of the emission from the

red fibrillary structures is at ca. 670 nm. This value matches the emission maxima of the cluster embedded in the gel measured by steady state fluorometry (in a cuvette) peaking at 672 nm (Figure 4).

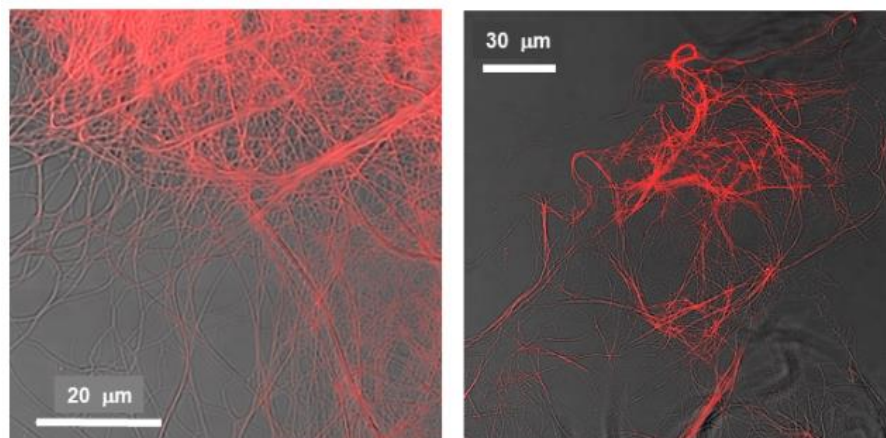


Figure 3. CLSM images showing the fibrillary network of **2** stained with molybdenum cluster **1**. $\lambda_{\text{ex}} = 488 \text{ nm}$, $\Delta\lambda = 590 - 730 \text{ nm}$. Conditions: $[\mathbf{2}] = 14.6 \text{ mM}$ (5 mg/mL), $[\mathbf{1}] = 0.25 \text{ mM}$ (0.5 mg/mL).

It is also worth to note that the spectrum of the hybrid gel (in a cuvette) is slightly blue-shifted as compared to the spectrum in pure dichloromethane (maximum at 682 nm, see Figure 4). This is a strong indication that cluster **1** is not freely moving in the solvent pools created by the entangled fibres of **2**, but stays in close contact with such structures, and the shift is a consequence of the different polarity of the environment where the cluster is entrapped. ESI-MS analysis of organogels containing 10% of cluster, both in DCM and in toluene, did not afford any peak corresponding to acetate exchange by molecules of gelator. In consequence we hypothesize that the interaction between clusters and fibres is supramolecular, with TBA cations playing an intercalation role (van der Waals forces would be responsible of the association between butyl chains of TBA and nonyl chains of gelator).

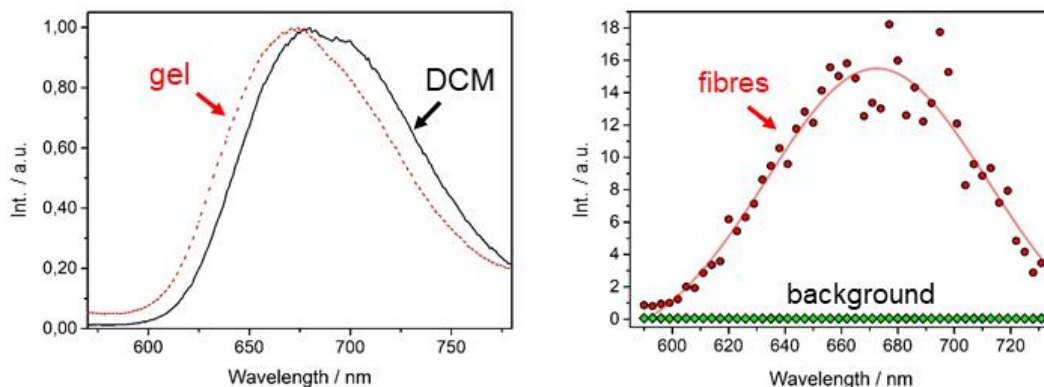


Figure 4 Left: phosphorescence emission measured *in cuvette* in a spectrofluorometer ($\lambda_{\text{ex}} = 400$ nm) of **1** in dichloromethane solution (black curve) and in gel formed by **2** (red dotted curve). Conditions: $[\mathbf{2}] = 14.6$ mM (5 mg/mL), $[\mathbf{1}] = 0.03$ mM (0.06 mg/mL). Right: phosphorescence emission of the red fibres measured in the confocal microscope along with the black background. Conditions: $[\mathbf{2}] = 14.6$ mM (5 mg/mL), $[\mathbf{1}] = 0.25$ mM (0.5 mg/mL).

Another feature that can be noticed in the spectrum of gel samples containing **1** is that it becomes sharper in comparison to **1** in DCM solution. As it can be seen in Figure 4 (left), the phosphorescence of **1** in solution is comprised by a broad band centered at 682 nm and a shoulder at ca. 700 nm. It has been reported that this multiple emission arises from the existence of several excited triplet states.^{50,51} It can be concluded that stacking of **1** to the gel fibres induces a redistribution of the relative contribution of each triplet state to the total emission.

The chromatic coordinates (CIE1931 standard) of the doped gel were calculated, resulting in $x = 0.725$ and $y = 0.274$, which qualifies the hybrid as a deep-red dye (requisite $x \geq 0.670$). The xerogel material, formed after evaporation of the solvent (Figure S3, Supporting Information), displayed coordinates $x = 0.713$ and $y = 0.268$. Chromatic diagrams of both organogel and xerogel can be seen in the Figure S2 of the Supporting

Information. Analogous (x,y) values have been reported for hexanuclear molybdenum complexes entrapped in organic polymers.²⁵ The photoluminescence quantum yield (PLQY) of gel and xerogel samples resulted 2.2 % and 6.1 %, respectively. Samples were measured in aerated conditions and hence those values reflect the quenching of the excited states by oxygen, leading to $^1\text{O}_2$. As a matter of fact, the most remarkable property of the organogels here reported is their ability to catalyze photo-oxygenations via the generation of $^1\text{O}_2$ upon illumination. In order to prove this property two benchmark oxidations were tested: the reaction of 9,10-dimethylantracene (DMA) with $^1\text{O}_2$ to yield the corresponding endoperoxide and the transformation of 1,5-dihydroxynaphthalene (DHN) to juglone (see reactions in Figure 5). In both cases the reactions were followed easily by means of UV-vis absorption spectroscopy, and the kinetic observed constants (k_{obs}) were calculated after fitting to a pseudo-first order model, according to the literature.³¹

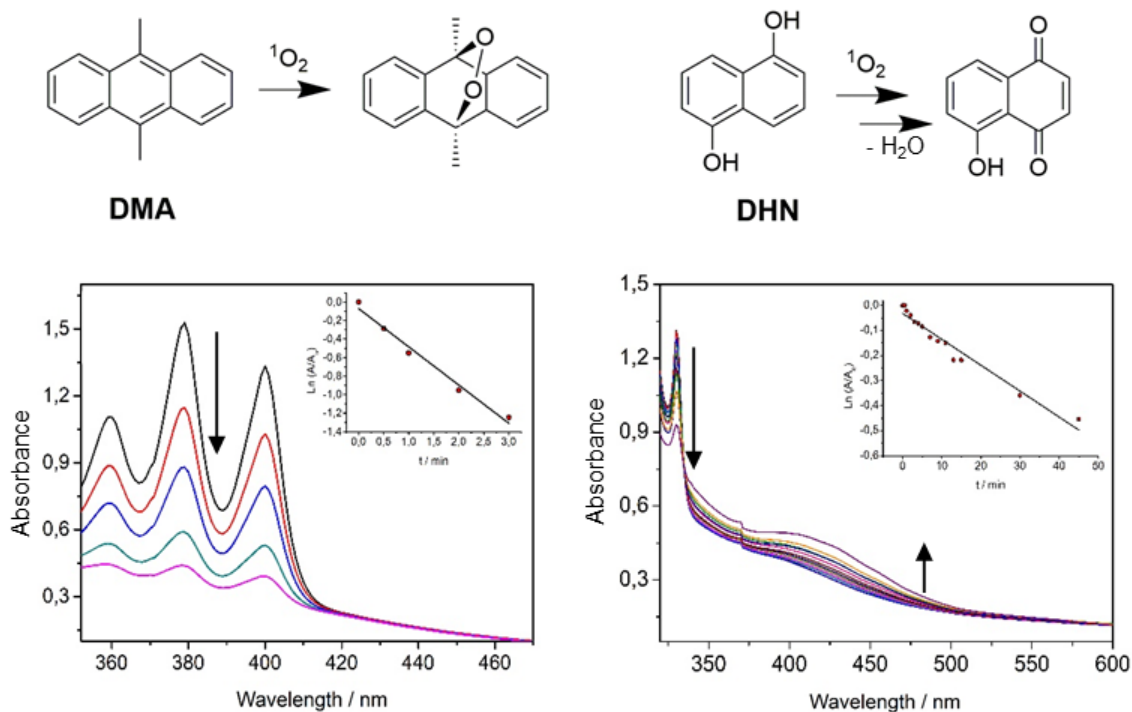


Figure 5. Illustrative UV-vis spectra monitoring the photo-oxygenation reactions of DMA (left) and DHN (right) photocatalyzed by **1** entrapped in a dichloromethane gel of **2**. Conditions: $[2] = 14.6 \text{ mM}$ (5 mg/mL), $[1] = 0.03 \text{ mM}$ (0.06 mg/mL).

A gel of **2** entrapping **1** in dichloromethane induces the photooxygenation of DMA at a remarkable rate of 0.415 min^{-1} . This value is not much lower than the value recorded in pure dichloromethane (0.563 min^{-1}). It must be taken into account that the photoactivity of supported photosensitizers, as described in the literature, drop drastically when immobilised on materials.¹⁷ Gels prepared in toluene also showed activity for the photooxidation of DMA, although in this case the difference between k_{obs} (gel) and k_{obs} (solution) was higher (0.042 vs 0.139 min^{-1} respectively) than in DCM. The higher reactivity in DCM as compared to toluene must be due to the different singlet oxygen lifetime in those solvents (91 us in DCM, 29 us in toluene).⁵² The reactivity of DHN to produce juglone also was measured in a DCM gel entrapping **1** ($k_{\text{obs}} = 0.010 \text{ min}^{-1}$) and for free **1** in DCM ($k_{\text{obs}} = 0.018 \text{ min}^{-1}$). LED lamps used for this study emit very low infrared radiation, so no increase of temperature of the gels took place during the reactions. See illustrative examples of irradiations in Figure 5 and all the kinetic values in Table 1. It must be noted that the comparison between rate constants here reported must be done with care since light scattering in the organogels made very difficult to assure that all samples absorbed the same number of photons (despite the concentration of cluster was the same in all cases). However, the kinetics here reported can serve as a qualitative confirmation that photochemical activity is maintained in the hybrid gels. As a matter of fact, the outcome of preparing gels doped with clusters was not predictable, since negative events such as cluster aggregation or decomposition, or quenching of the excited state by the fibres, could have taken place, which was not the case.

Table 1. Pseudo-first order kinetic constants for the oxygenation of DMA and DHN in gel and in solution.

Substrate	Sample	Solvent	$k_{\text{obs}} \cdot 10^3 \text{ (min}^{-1}\text{)}$
DMA	1 in gel	DCM	415 ± 33
DMA	1 in solution	DCM	563 ± 36
DMA	Solution blank	DCM	6.2 ± 0.4
DMA	Gel blank	DCM	17 ± 2
DMA	1 in gel	Toluene	42.5 ± 0.4
DMA	1 in solution	Toluene	139 ± 2
DMA	Solution blank	Toluene	0.6 ± 0.8
DMA	Gel blank	Toluene	1 ± 3
DHN	1 in gel	DCM	10.3 ± 0.6
DHN	1 in solution	DCM	18 ± 1
DHN	Solution blank	DCM	0.6 ± 0.1
DHN	Gel blank	DCM	4.2 ± 0.5

Conditions: $[\mathbf{2}] = 14.6 \text{ mM}$ (5 mg/mL), $[\mathbf{1}] = 0.03 \text{ mM}$ (0.06 mg/mL), $[\text{DMA}] = [\text{DHN}] = 0.1 \text{ mM}$. Aerated dichloromethane or toluene were used as solvents. $T = 25 \text{ }^\circ\text{C}$. Blanks show minor reactivity due to self-photosensitization.

In summary, a molecular organogel has been used for the first time as support for a photoactive hexanuclear molybdenum cluster cluster of formula $\text{TBA}_2[\text{Mo}_6\text{I}_8\text{Ac}_6]$ (TBA = tetrabutylammonium, Ac = acetate). Electron and confocal microscopic analyses showed the alignment of the nanoclusters of **1** to the 1D self-assembled fibres formed by **2** and fluorescence spectroscopy corroborated the interaction of the emissive clusters with the fibres. The new hybrid system is a deep-red emissive material (phosphorescence maximum at ca. 680 nm), with chromatic coordinates $x=0.725$, $y=0.274$, capable of generating efficiently $^1\text{O}_2$ upon illumination with white light. Photo-oxygenation reaction rates (substrates 9,10-dimethylantracene and 1,5-dihydroxynaphthalene) recorded in gel state, in dichloromethane, were of the same order of

magnitude as those recorded in solution. The results here presented can be inscribed within the emerging field of intra-gel photochemistry.⁵³⁻⁵⁶ A practical advantage of the gel-photosensitizer systems here presented could be the potential induction of regio- and stereoselectivity if oxygenations take place close to the fiber. In this case, the fibrillary network would be acting as a templating agent. It must be recalled that self-assembled fibrillary networks made with amino acid derivatives, present chirality, so it is expected that association of the appropriate substrate to the photosensitizing chiral fiber would give rise to a preferential oxygenation mode. Few examples of selective photooxygenations have been presented in the literature, for instance, using amino acids, zeolites or metallic complexes.⁵⁷⁻⁶⁰ Current work is in progress along this direction using substrates prone to association with the self-assembled gelator.

ASSOCIATED CONTENT

Supporting Information

Experimental section, melting curves, xerogel pictures, EDS analyses and additional TEM / STEM pictures.

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CONFLICTS OF INTEREST

There are no conflicts to declare.

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