Supporting Information

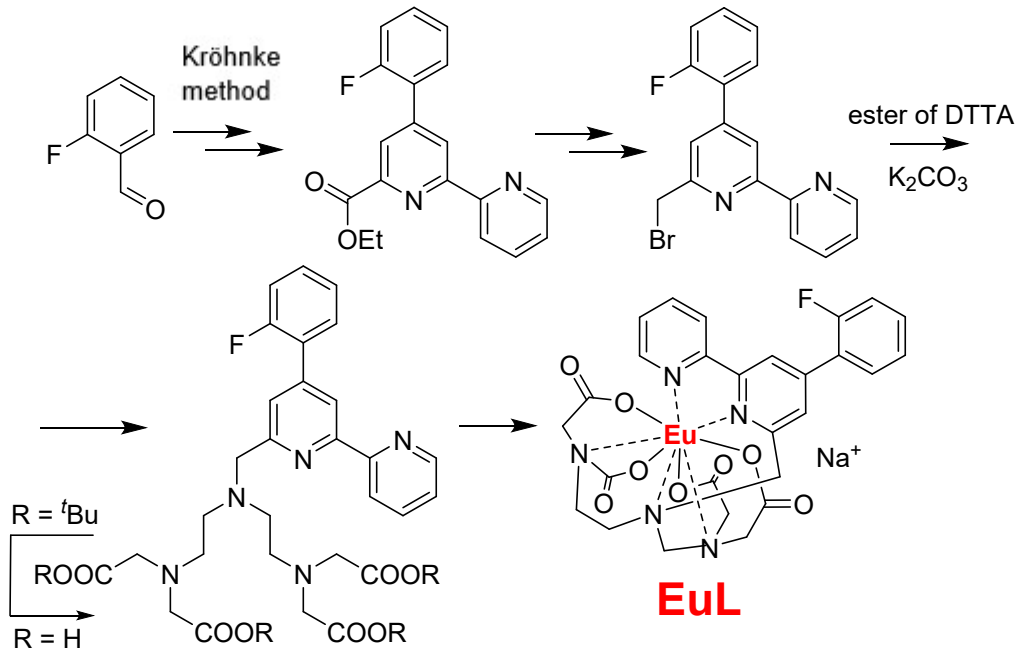
Polyacrylamide-Chitosan semi-interpenetrating self-healing network with embedded Keplerate $\{Mo_{132}\}$ for pH-controlled release of Eu-fluorescent tag

Kirill Grzhegorzhevskii[a,b*], Ekaterina Rudakova[a], Alexey Krinochkin[a,b], Dmitry Kopchuk[a,b], Yaroslav Shtaitz[a,b], Lidia Adamova[a], Grigory Kim[a,b], Elena Rusinova[a] and Alisa Shmidt[a]

[a]*Ural Federal University named after the first President of Russia B.N. Yeltsin, 19 Mira str., 620002, Ekaterinburg, Russia*

[b]*I. Ya. Postovsky Institute of Organic Synthesis, Ural branch of RAS, 22/20 S. Kovalevskoy/Akademicheskaya str., 620990, Ekaterinburg, Russia*

[*] *Corresponded author: kirillvalentinovich@urfu.ru*



Scheme S1. General scheme for the synthesis of the complex $Eu^{III}L$.

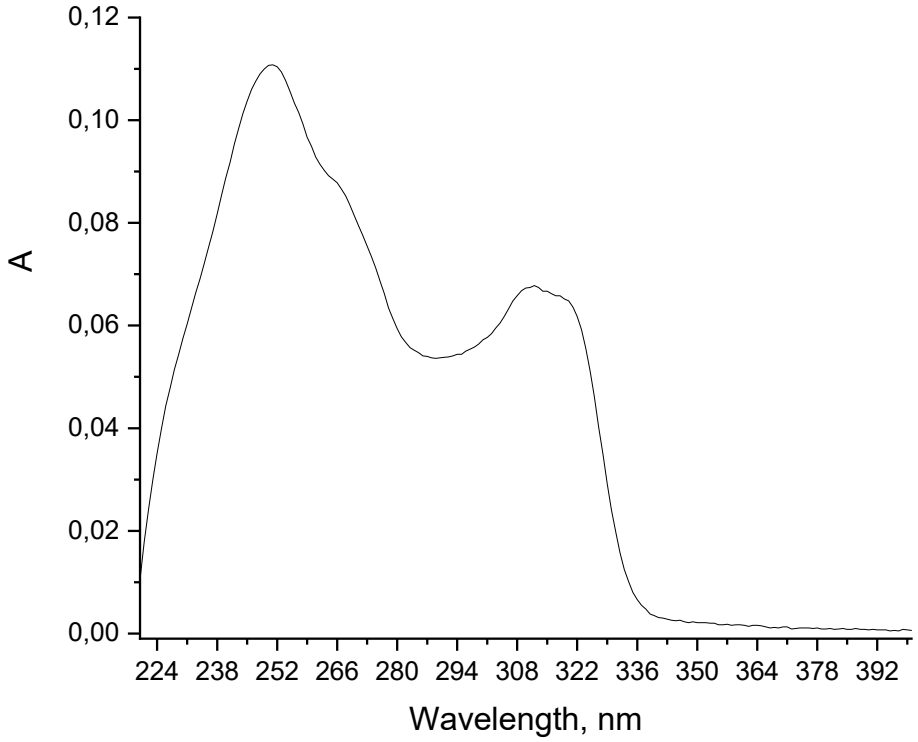


Figure S1. Absorption spectrum of $Eu^{III}L$ in water at room temperature.

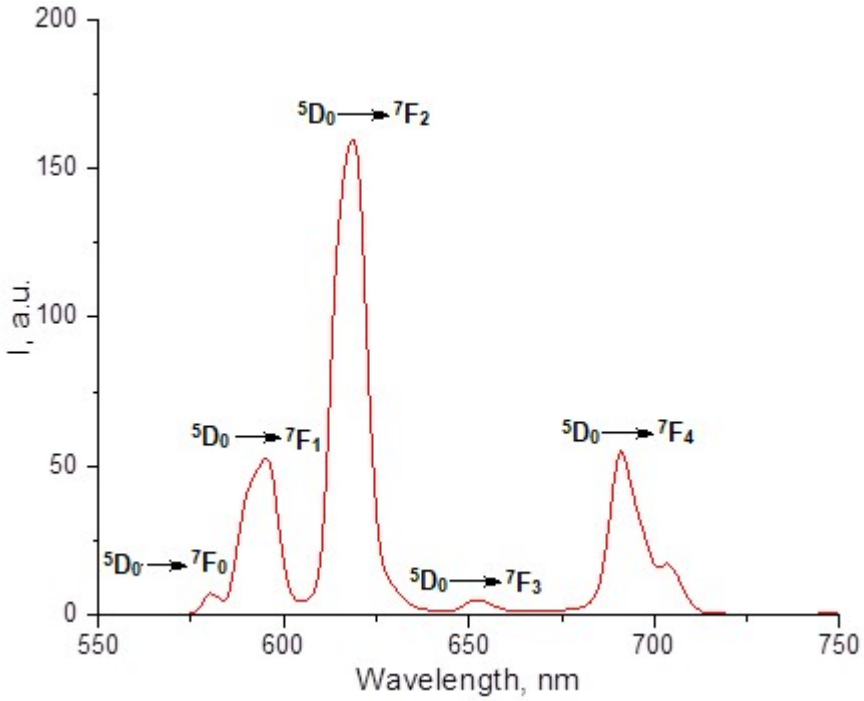
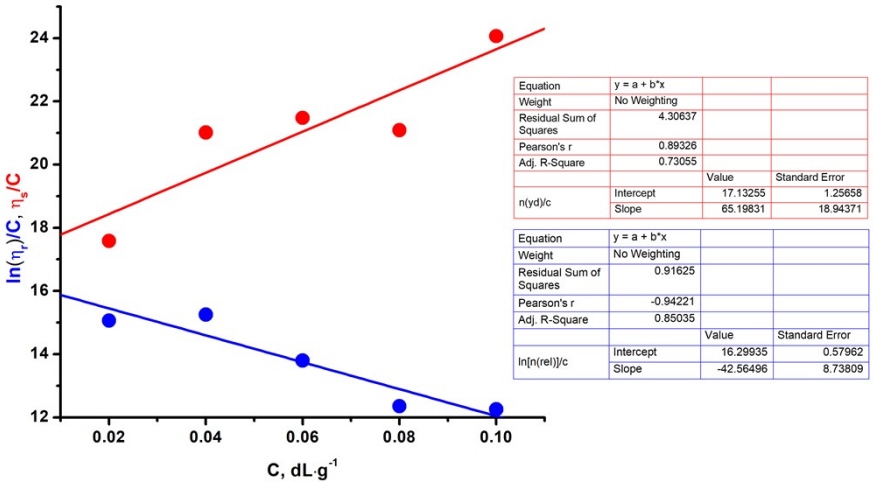


Figure S2. Europium(III) cation luminescence spectrum of complex $Eu^{III}L$ (excitation at 312 nm).

Table S1. The photophysical properties of complex $Eu^{III}L$

λ_{max}, nm[a]	E[b], 10^{-3} $M^{-1}cm^{-1}$	Φ_{Ln}, %[c]	τ_{H2O}, ms[d]	τ_{D2O}, ms[e]	Q[f]
251, 267, 274 $_{sh}$, 312, 322$_{sh}$	8.9	16.2	1.07	1.86	0.18

[a]Absorption maxima in H_2O at room temperature; [b]The molar extinction coefficient corresponds to the longest absorption wavelength; [c]Lanthanide luminescence quantum yields in water solution were determined using $[Ru(bpy)_3]Cl_2$ (Φ = 0.04 in aerated water[1]); [d]Lanthanide luminescence lifetime in water; [e]Lanthanide luminescence lifetime in D_2O; [f]The number of coordinated water molecules was calculated using the formula[2]: $q_{Eu} = 1.2*(1/\tau_{H2O} - 1/\tau_{D2O} - 0.25)$.



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	4.30637		
Pearson's r	0.89326		
Adj. R-Square	0.73055		
		Value	Standard Error
n(yd)/c	Intercept	17.13255	1.25658
	Slope	65.19831	18.94371

Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0.91625		
Pearson's r	-0.94221		
Adj. R-Square	0.85035		
		Value	Standard Error
ln[n(rel)]/c	Intercept	16.29935	0.57962
	Slope	-42.56496	8.73809

Figure S3. The dependency of η_r/C and $\ln(\eta_s)/C$ on PAAm3 concentration in water.

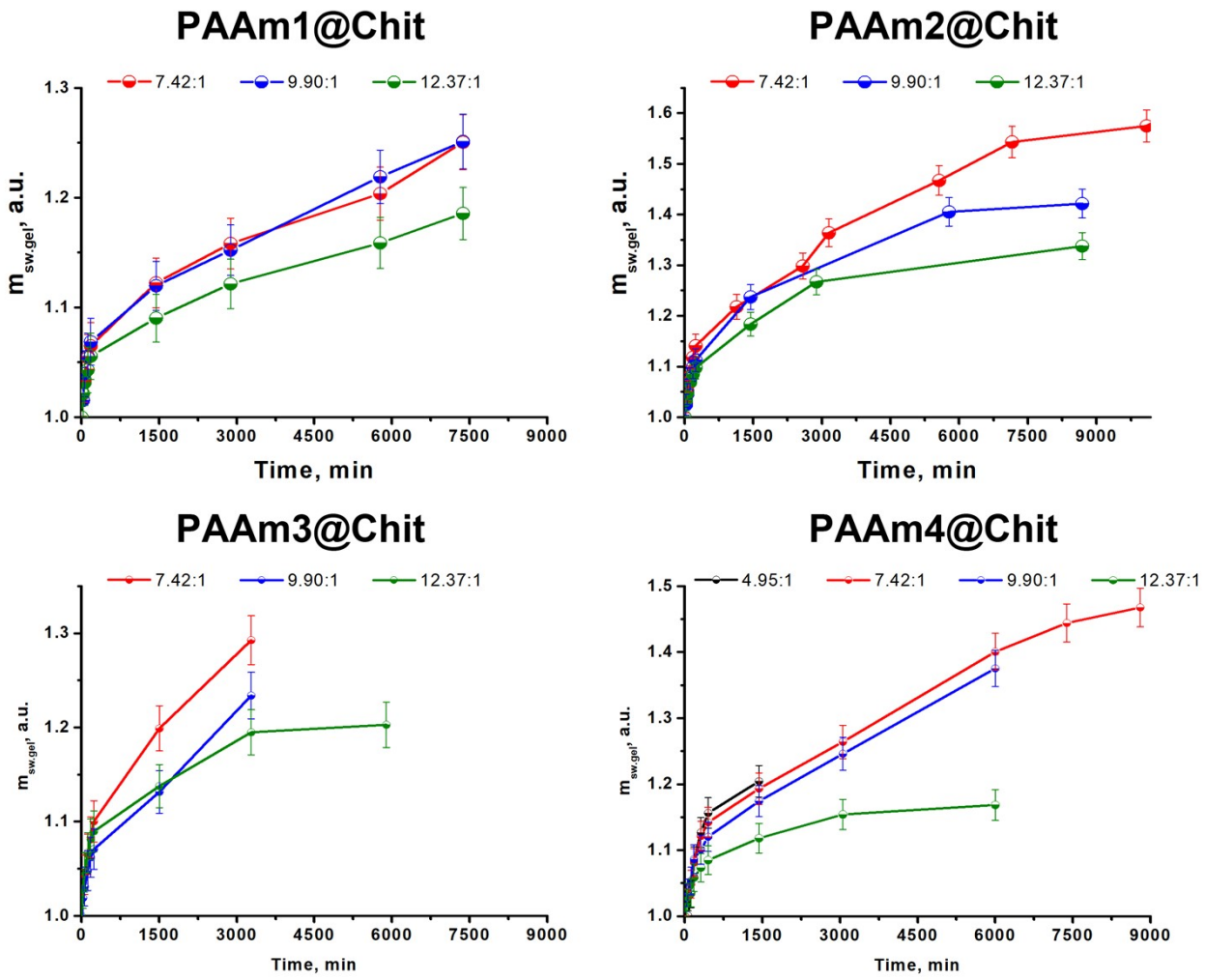


Figure S4. The swelling kinetics of PAAm@Chit hydrogels prepared with different molecular weights of PAAm: PAAm1 (0.67 MDa), PAAm2 (1.5 MDa), PAAm3 (5.95-6 MDa), and PAAm4 (10.8-11.4 MDa) where the C_{PAAm} is 3.175, 5.925, 5.6, and 6.35 $g \cdot L^{-1}$, respectively.

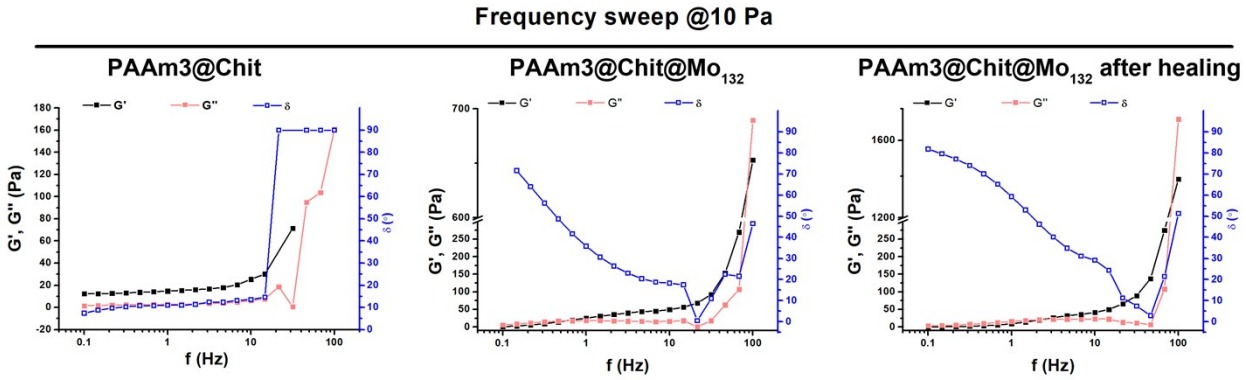


Figure S5. The frequency sweep dependency of the storage (G´) and loss (G´´) modules on the hydrogel composition (blank and POM-embedded) and self-healing process measured at 10 Pa shear stress.

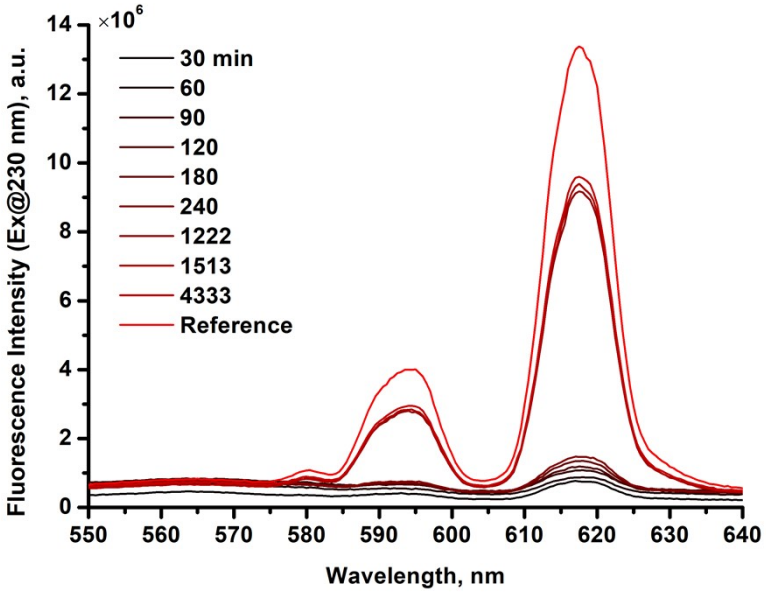


Figure S6. The steady-state fluorescence measurement of the aliquot samples from the receiver (solution) during the releasing experiments of PAAm3@Chit@Mo_{132} loaded with $Eu^{III}L$. Reference corresponds to the highest possible concentration of the $Eu^{III}L$ in the 250 mL in accordance with its moles loaded in hydrogel (i.e. 4.186×10^{-5} mol·L^{-1}).

References

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2 A. Beeby, I. M. Clarkson, R. S. Dickins, S. Faulkner, D. Parker, L. Royle, A. S. de Sousa, J. A. G. Williams and M. Woods, *J. Chem. Soc. Perkin Trans. 2*, 1999, **2**, 493–504.