IOCB 2024 Conference

The 1st International Online Conference on Biomimetics

15–17 May 2024 | Online

Bioinspired self-healing luminescent lanthanide bipyridinedicarboxiamide complexes

Anna S. Miroshnichenko[1,2] Ivan S. Mukhin[2,3], Regina M. Islamova[1]

1 St. Petersburg University, 7/9 Universitetskaya nab., St. Petersburg 199034, Russia

2 Laboratory of Renewable Energy Sources, St. Petersburg Academic University, 8/3 Khlopina Str., St. Petersburg 194021, Russia

3 High School of Engineering Physics, The Great St. Petersburg Polytechnical University, 29 Polytechnicheskaya Str., St. Petersburg 195251, Russia

INTRODUCTION & AIM

Polymers with photoluminescent centers in their structure and self-healing properties are of great interest in the field of bioimaging and could be artificial analogs to green fluorescent protein (**GFP**) as jellyfish demonstrate intrinsic photoluminescence along with self-healing of their organs [1-2].

Polymer metal complexes (**PMCs**) based on europium(III) and terbium(III)- containing polysiloxanes could be artificial analogs to **GFP** due to their excellent luminescent and self-healing properties.

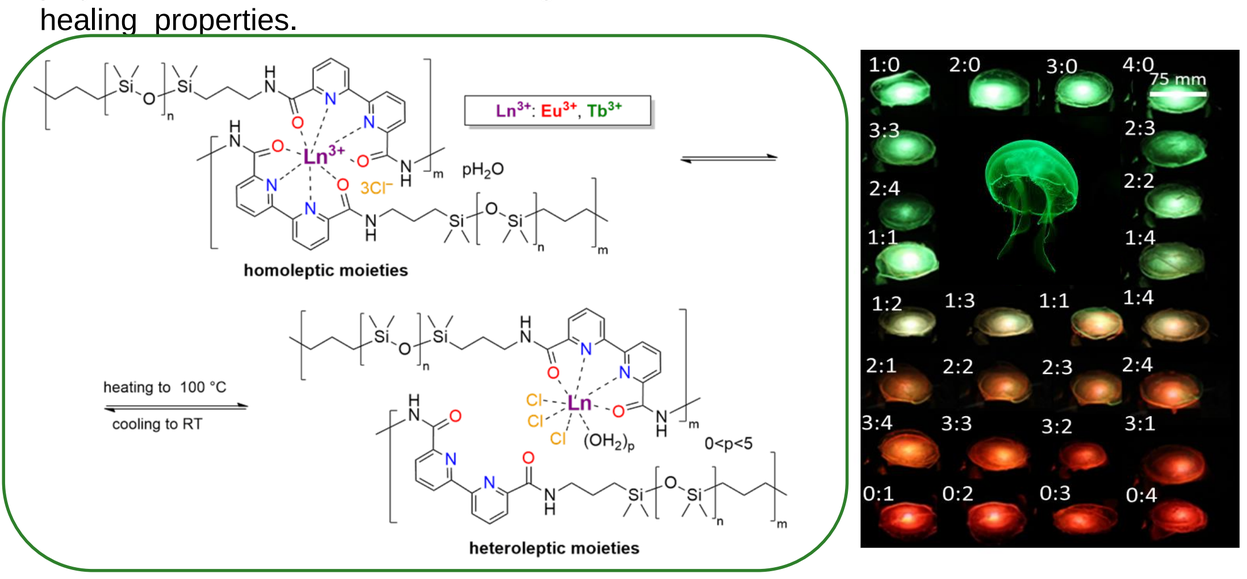

Figure 1 – Suggested self-healing mechanism of **Ln–Bipy–PDMS (left)** and optical image of staked **Ln–Bipy–PDMS** with different type of lanthanide (**right**) (insert shows optical image of jellyfish)

In addition, low-molecular complexes **[Tb(BDCA)$_2$(H$_2$O)]Cl$_3$** and **[Eu(BDCA)$_2$(H$_2$O)]Cl$_3$** could be used as fillers for other bioinert polymer matrixes like polyethylene glycol (PEG) and used in bioimaging and ect.

Materials and Methods

Self-healing luminescent silicone rubbers were obtained in two steps (**Figure 2**). At first stage 2,2'-bipyridine-6,6'-dicarboxamide-*co*-polydimethylsiloxanes (**Bipy-PDMS5000** and **Bipy-PDMS25000**) were synthesized by a polycondensation reaction between 2,2'-bipyridine-6,6'-dicarboxylic acid dichloride and *α,ω*-di(3-aminopropyldimethylsiloxy)polydimethylsiloxanes (**APDMS**) with a number average molecular weight M_n = 5000 and 25000, respectively. Cross-linked silicone materials were obtained by the reaction of complex formation of **Bipy–PDMS** obtained by and the chloride of the corresponding lanthanide(III) — $EuCl_3$ and $TbCl_3$.

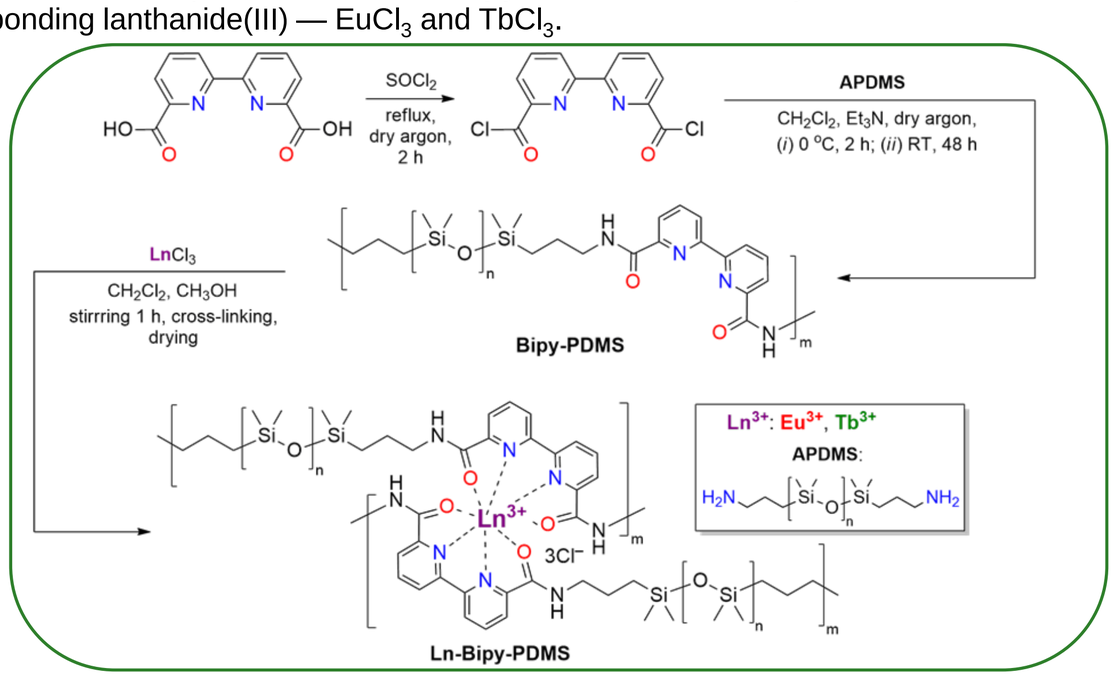

Figure 2 – Scheme of **Ln-Bipy-PDMS** synthesis

[Eu(BDCA)$_2$(H$_2$O)]Cl$_3$ and **[Tb(BDCA)$_2$(H$_2$O)]Cl$_3$** were synthesized at room temperature from *N*^{6},*N*^{6}–diisopropyl–2,2'–bipyridine–6,6'-dicarboxamide (**BDCA**) and anhydrous europium(III) and terbium(III) chlorides using the dichloromethane and methanol (**Figure 3**).

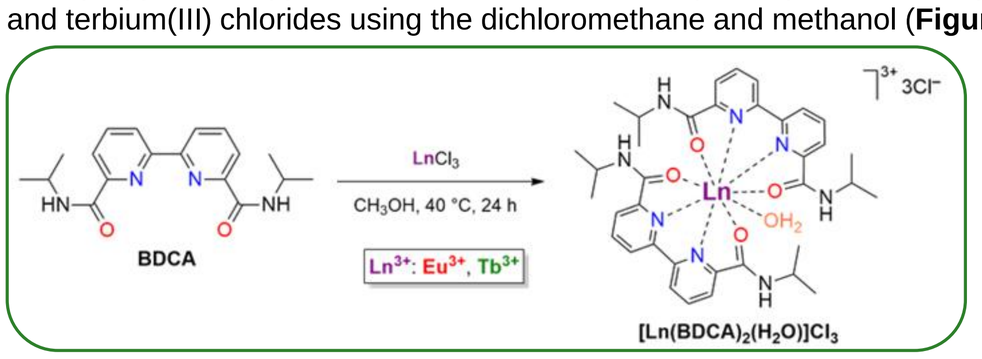

Figure 3 – Scheme of **[Eu(BDCA)$_2$(H$_2$O)]Cl$_3$** and **[Tb(BDCA)$_2$(H$_2$O)]Cl$_3$** synthesis

RESULTS & DISCUSSION

PMCs have relatively high strength characteristics tensile strength *σ* and Young's modulus *E* and reach values of 1.6 and 3.6 MPa, respectively. At the same time, relative elongation at break *ε* values reach 185–255%. Self-healing efficiency (*η*) exceed 85%. within 48 hours (2 days) at 100°C.

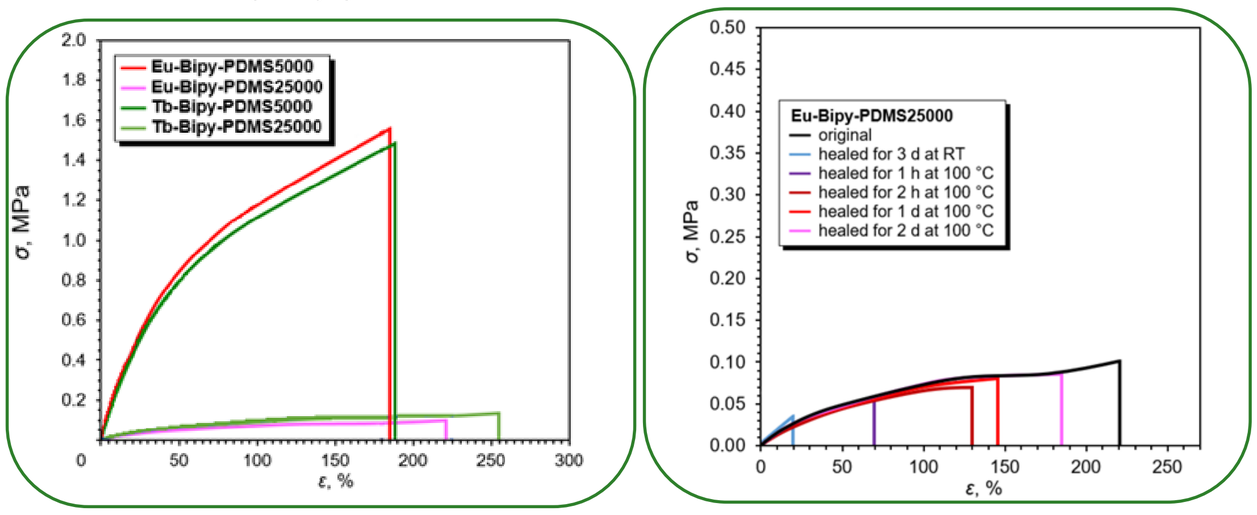

Figure 4 – Stress–strain curves of PMCs **(left)** and of self-healed **Eu–Bipy–PDMS25000** at 100°C **(right).** Stretching speed 40 mm·min^{-1}. Sample form according to ISO 37 type 3

Under UV excitation (λ_{ex}=340 nm) **PMCs**, **[Tb(BDCA)$_2$(H$_2$O)]Cl$_3$** and **[Eu(BDCA)$_2$(H$_2$O)]Cl$_3$** demonstrate bright photoluminescence of Eu^{3+} and Tb^{3+} ions characteristic spectral lines in the red and green region of the spectrum (**Figure 5**).

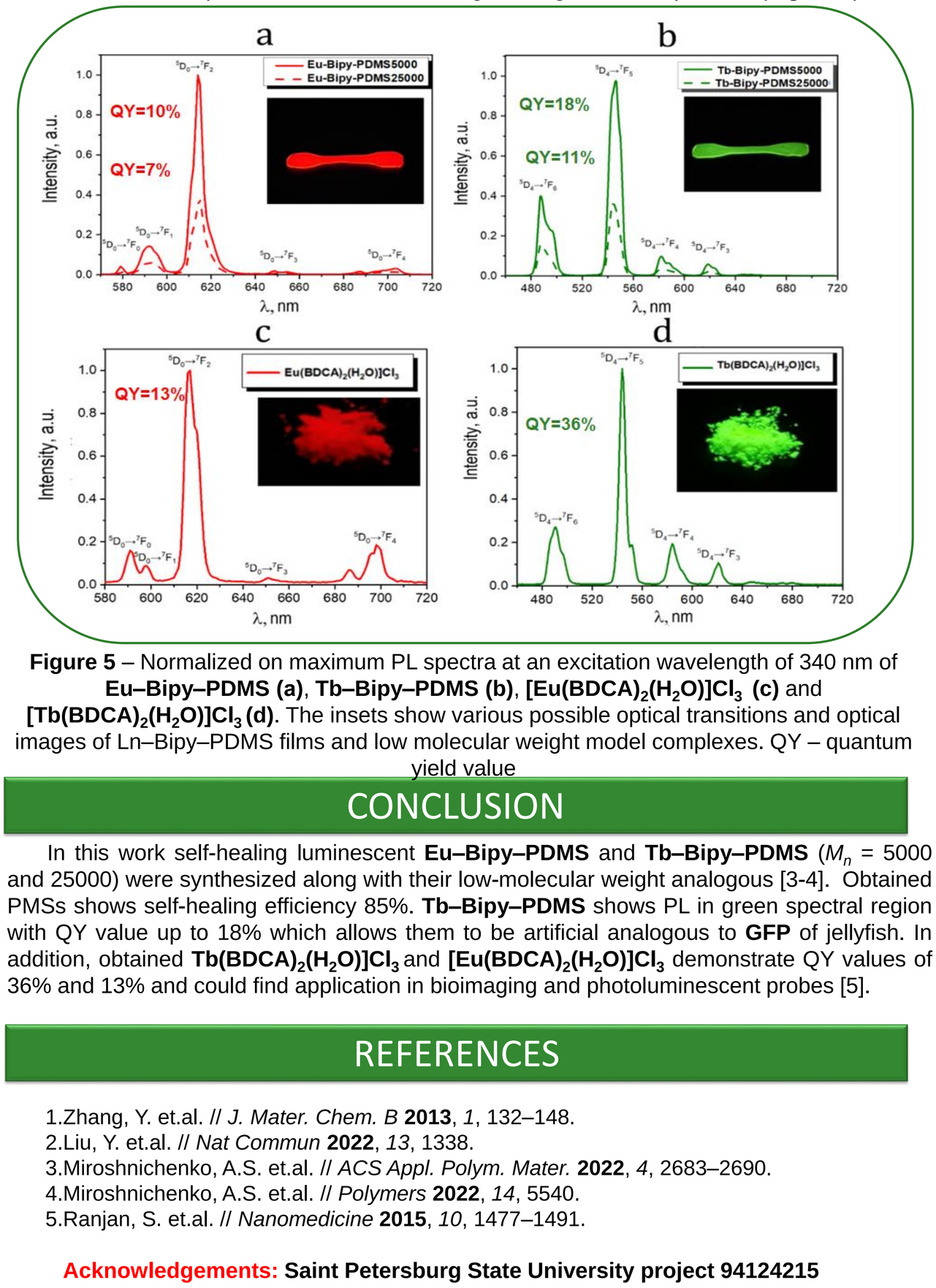

Figure 5 – Normalized on maximum PL spectra at an excitation wavelength of 340 nm of **Eu–Bipy–PDMS (a)**, **Tb–Bipy–PDMS (b)**, **[Eu(BDCA)$_2$(H$_2$O)]Cl$_3$ (c)** and **[Tb(BDCA)$_2$(H$_2$O)]Cl$_3$ (d)**. The insets show various possible optical transitions and optical images of Ln–Bipy–PDMS films and low molecular weight model complexes. QY – quantum yield value

CONCLUSION

In this work self-healing luminescent **Eu–Bipy–PDMS** and **Tb–Bipy–PDMS** (M_n = 5000 and 25000) were synthesized along with their low-molecular weight analogous [3-4]. Obtained PMSs shows self-healing efficiency 85%. **Tb–Bipy–PDMS** shows PL in green spectral region with QY value up to 18% which allows them to be artificial analogous to **GFP** of jellyfish. In addition, obtained **Tb(BDCA)$_2$(H$_2$O)]Cl$_3$** and **[Eu(BDCA)$_2$(H$_2$O)]Cl$_3$** demonstrate QY values of 36% and 13% and could find application in bioimaging and photoluminescent probes [5].

REFERENCES

1.Zhang, Y. et.al. // *J. Mater. Chem. B* **2013**, *1*, 132–148.
2.Liu, Y. et.al. // *Nat Commun* **2022**, *13*, 1338.
3.Miroshnichenko, A.S. et.al. // *ACS Appl. Polym. Mater.* **2022**, *4*, 2683–2690.
4.Miroshnichenko, A.S. et.al. // *Polymers* **2022**, *14*, 5540.
5.Ranjan, S. et.al. // *Nanomedicine* **2015**, *10*, 1477–1491.

Acknowledgements: **Saint Petersburg State University project 94124215**