Electronic Supplementary Information

Luminescence and energy transfer mechanisms in photo-thermorefractive glasses co-doped with silver molecular clusters and Eu³⁺

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Figure S1. (a) Absorbance spectra of initial and ion-exchanged Sb0Eu1 glass samples before and after the heat treatment during 24 hours (the treatment temperatures are indicated on the graph). (b) Emission spectra of the initial (λ_{ex} =350 nm, λ_{ex} =365 nm) and ion-exchanged Sb0Eu1 glass samples before and after the heat treatment (λ_{ex} =350 nm).



Figure S2. Absorbance spectra of the initial and ion-exchanged Sb2Eu1 (a), Sb2Eu5 (b) glass samples before and after the heat treatment at 350–500 °C. Emission spectra (λ_{ex} =350 nm) of the initial and ion-exchanged Sb2Eu1 (c), Sb2Eu5 (d) glass samples before and after the heat treatment at 350–500 °C. The treatment temperature values are indicated on the graph, duration is 24 hours.



Figure S3. QY of ion-exchanged PTR glasses Sb2Eu0 (a), Sb2Eu1 (b), Sb2Eu5 (c) vs. temperature and duration of the heat treatment. Squares represent experimental data.



Figure S4. Comparison of ion-exchanged and heat-treated Sb2Eu0 glass luminescence spectra obtained from fluorometer and integrating sphere setup, $\lambda_{ex} = 340$ nm.



Figure S5. Normalized phosphorescence spectra of ion-exchanged and heat-treated Sb2Eu0, Sb2Eu1, and Sb2Eu5 glasses collected with fixed gate time and delay time of (a) 80 μ s, (b) 140 μ s, (c) 300 μ s. λ_{ex} =340 nm.

Förster distance calculation

The value of Förster distance was calculated using standard equation.¹

$$R_0^6 = \frac{9(\ln 10)k^2 \Phi_0}{128\pi^5 N_A n^4} \int F_\lambda(\lambda) \varepsilon(\lambda) \lambda^4 d\lambda$$

, where Φ_0 – fluorescence quantum yield of SMCs in the absence of Eu³⁺. k – orientation factor. N_A – Avogadro constant. n – refractive index of medium. $F_{\lambda}(\lambda)$ – SMCs fluorescence spectrum, normalized to unit area. $\varepsilon(\lambda)$ – decadic molar absorption coefficient of Eu³⁺ ions. λ – wavelength.

Widely used value of 2/3 for k^2 is valid only for the case of fast fluorophore rotation in liquid solutions. k^2 value of 0.4762 was used to describe random distribution of static donors and acceptors.²

- 1. S.E. Braslavsky, E. Fron, H.B. Rodríguez, E.S. Román, G.D. Scholes, G. Schweitzer, B. Valeur and J. Wirz, *Photochem. Photobiol. Sci.*, 2008, **7**, 1444–1448.
- 2. I. Medintz and N. Hildebrandt, *FRET Förster Resonance Energy Transfer*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2014.