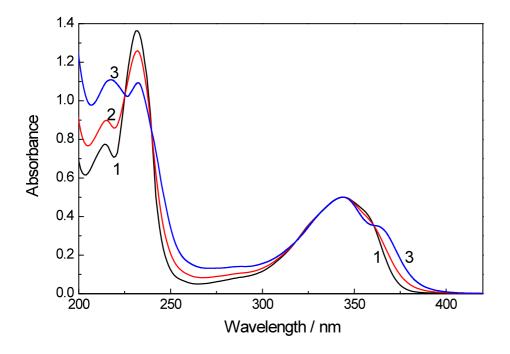
## Photophysics of 1,8-naphthalimide / Ln(III) dyads (Ln = Eu, Gd): napthalimide → Eu(III) energy-transfer from both singlet and triplet states.

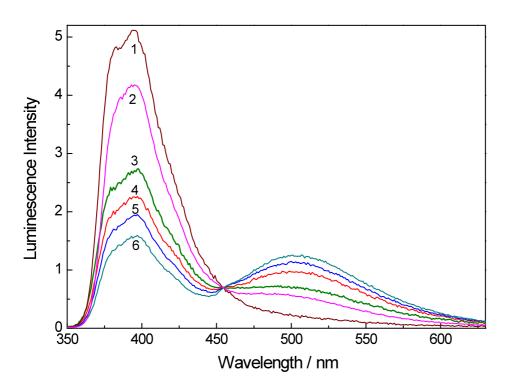
Victor F. Plyusnin,<sup>*a*,\*</sup> Arkady S. Kupryakov, <sup>*a*</sup> Vyacheslav P. Grivin, <sup>*a*</sup> Alexander H. Shelton, <sup>*b*</sup> Igor V. Sazanovich, <sup>*b*</sup> Anthony J. H. M. Meijer, <sup>*b*</sup> Julia A. Weinstein <sup>*b*</sup> and Michael D. Ward <sup>*b*,\*</sup>

Electronic supporting information

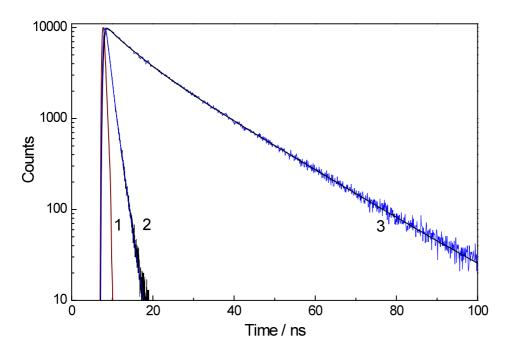
Figures S1 – S7: Additional figures (absorption spectra, luminescence spectra, kinetic traces, triplet-triplet absorption spectra) for the three compounds.



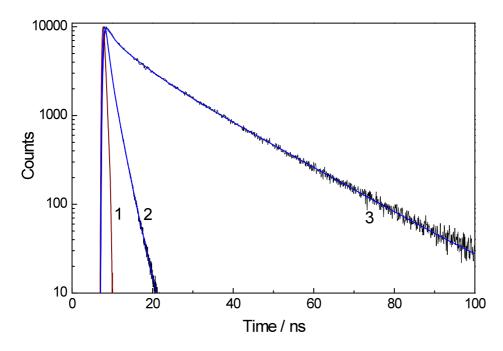
**Fig. S1.** UV/Vis absorption spectra of Gd•L in water: (1) concentration  $4.27 \times 10^{-5}$  M (path length 1 cm); and (2) concentration  $0.79 \times 10^{-2}$  M (path length 54 µm). The calculated spectrum of a dimer is presented as curve (3).



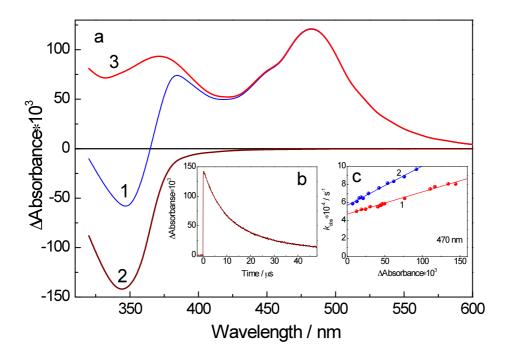
**Fig. S2.** Luminescence spectra of Gd•L in water with excitation a 320 nm. Spectra (1) – (6) were recorded at concentrations  $1.14 \times 10^{-4}$ ,  $1.37 \times 10^{-3}$ ,  $2.04 \times 10^{-3}$ ,  $4.52 \times 10^{-3}$ ,  $7.43 \times 10^{-3}$  and  $1.02 \times 10^{-2}$  M, respectively. Spectra (1) and (2) were recorded using 1 and 0.1 cm cuvettes; spectra (3) – (6) were recorded using a 54 µm cuvette. Normalization of spectra recorded with different path lengths was made with the help of the isosbestic point.



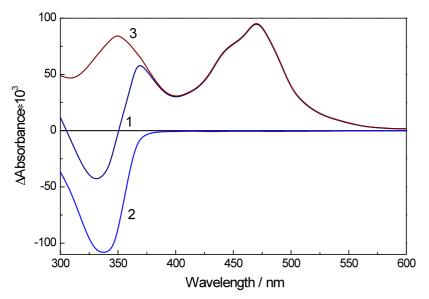
**Fig. S3.** Luminescence decay kinetics of Eu•L in water with excitation at 320 nm. Curve (1): instrument response function. Curves (2) and (3): decay kinetics at 395 and 505 nm, respectively (Eu•L concentration,  $1.75 \times 10^{-2}$  M; 54 µm cuvette). Solid lines on the kinetic traces are the calculated fits using a three exponential approximation (parameters in Table 1).



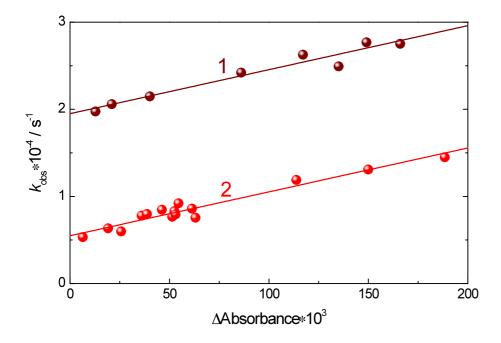
**Fig. S4.** Luminescence decay kinetics of Gd•L in water with excitation at 320 nm. Curve (1): instrument response function. Curve (2): decay kinetics at 393 nm at low Gd•L concentration  $(1.13 \times 10^{-4} \text{ M}, 1 \text{ cm} \text{ cuvette})$ . Curve (3): decay kinetics at 500 nm at high Gd•L concentration  $(7.9 \times 10^{-3} \text{ M}, 54 \text{ µm} \text{ cuvette})$ . Solid lines on the kinetic traces are the calculated fits using a three exponential approximation (parameters in Table 1).



**Fig. S5.** The triplet-triplet absorption spectrum (**a**) and its decay (**b**) of Gd•L in deoxygenated water after laser excitation at 355 nm. Panel (**c**) shows the dependence of  $k_{obs}$  for the T-T absorption decay at 470 nm on the value of the initial absorption ( $\Delta A$ ), for both Gd•L (line 1) and Eu•L (line 2). In frame (**a**): (1), the measured differential T-T absorption; (2), the UV/Vis spectrum of the complex showing the naphthalimide absorption; (3), the difference between (1) and (2), *i.e.* the T-T absorption spectrum.



**Fig. S6.** The triplet-triplet absorption spectrum of Eu•L in deoxygenated CH<sub>3</sub>CN after laser excitation at 355 nm. Curve (1) is the measured differential T-T absorption; curve (2) is the UV/Vis spectrum of the complex showing the naphthalimide absorption; curve (3) is the difference between (1) and (2), *i.e.* the T-T absorption spectrum.



**Fig. S7.** Dependence of  $k_{obs}$  for the T-T absorption decay at 470 nm on the value of initial absorption ( $\Delta A$ ) for Eu•L (line 1) and Gd•L (line 2) in CH<sub>3</sub>CN.