

Large enhancement of the luminescence properties of an Eu(III) dye upon association with the DNA-CTMA matrix

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Contents

I. General Information	S1
II. Photophysical data in solution	S2
III. Photophysical data in thin films	S3
IV. References	S8

I. General Information

Luminescence measurements were carried out on quartz substrate.

Absolute photoluminescence quantum yield (Φ) for thin film was measured using a C11347 Quantaaurus Hamamatsu Photonics K.K spectrometer. A description of the experimental setup and measurement method can be found in the article of K. Suzuki et al [1]. Φ was calculated through Equation:

$$\Phi = \frac{PN(Em)}{PN(Abs)} = \frac{\int \frac{\lambda}{hc} [I_{em}^{sample}(\lambda) - I_{em}^{reference}(\lambda)] d\lambda}{\int \frac{\lambda}{hc} [I_{exc}^{sample}(\lambda) - I_{exc}^{reference}(\lambda)] d\lambda}$$

where PN(Em) is the number of emitted photons, PN(Abs) the number of absorbed photons, λ the wavelength, h the Planck's constant, c the speed of light, I_{em}^{sample} and $I_{em}^{reference}$ the photoluminescence intensities of the sample and reference, I_{exc}^{sample} and $I_{exc}^{reference}$ the excitation light intensities of the sample and reference. PN(Em) is calculated in the wavelength interval $[\lambda_i, \lambda_f]$, where λ_i is taken at about 10 nm above the excitation wavelength, while λ_f is the upper end wavelength in the emission spectrum. The error made was estimated at around 5%.

Time-resolved fluorescence curves were fitted by a multi-exponential function:

$$I(t) = \sum_{i=1}^m \alpha_i \exp\left(\frac{-t}{\tau_i}\right)$$

where m is the number of exponentials, α_i is the pre-exponential factor and τ_i is the lifetime of the component i . The quality of the fit was evaluated through the reduced χ^2 value.

In case of multi-exponential decay, it is possible to define an average lifetime as:

$$\tau_{av} = \frac{\sum_{i=1}^m \alpha_i \tau_i^2}{\sum_{i=1}^m \alpha_i \tau_i} \quad m = \text{multi-exponential decay number of the fit.}$$

II. Photophysical data in solution

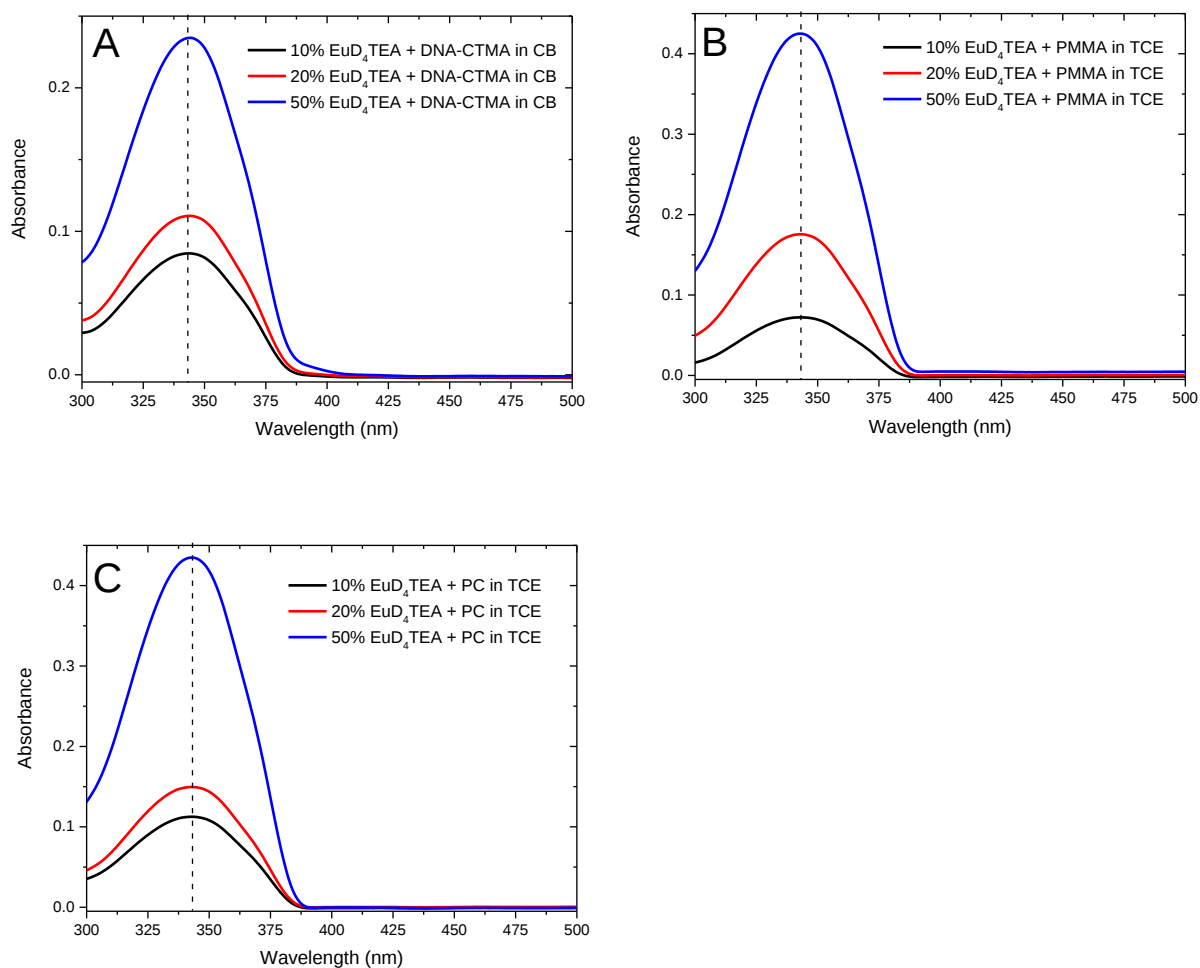


Figure S1. Panel A,B and C: solutions of EuD_4TEA complex at different concentrations in the TCE and CB solvents in presence of DNA-CTMA, PMMA and PC polymers, respectively.

III. Photophysical data in thin films

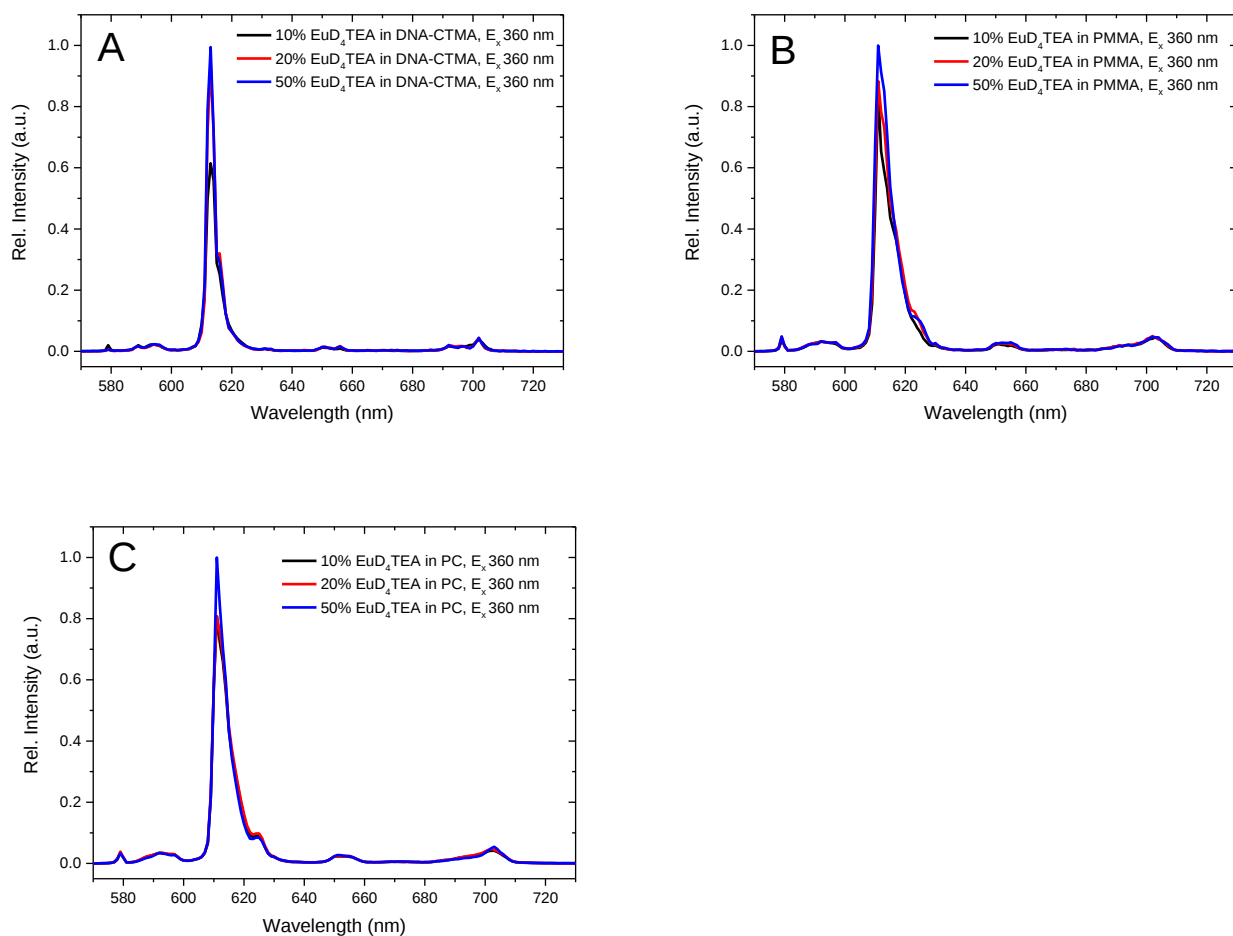


Figure S2. Panel A, B, and C emission spectra of thin films of the EuD₄TEA complex at various concentrations in DNA-CTMA, PMMA and PC matrices, respectively. For all three matrixes, the spectra have been scaled such that the respective ⁵D₀ → ⁷F₁ bands have identical areas.

Since the ⁵D₀ → ⁷F₁ transition is a magnetic dipole, whose intensity is largely independent of the environment of the Eu³⁺ ion, it can be used as an “internal reference”. Therefore, for all three matrixes, in order to compare different emission spectra, the latter have been scaled in such a way that the respective ⁵D₀ → ⁷F₁ bands have identical areas, see Figure S2.

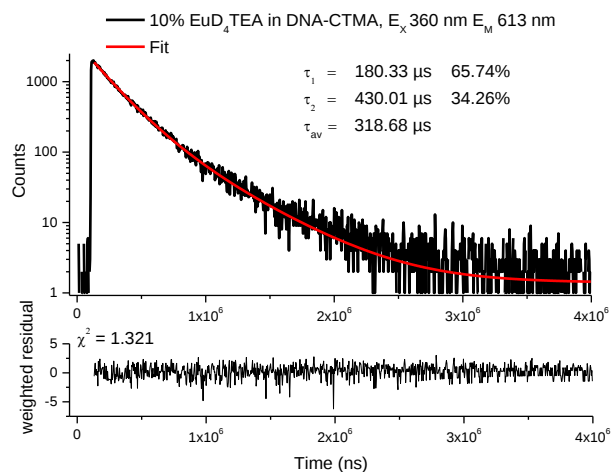


Figure S3. Time-resolved fluorescence decays and the relative fit of 10 % EuD₄TEA complex in the DNA-CTMA matrix. Emission wavelength 613 nm, excitation wavelength 360 nm.

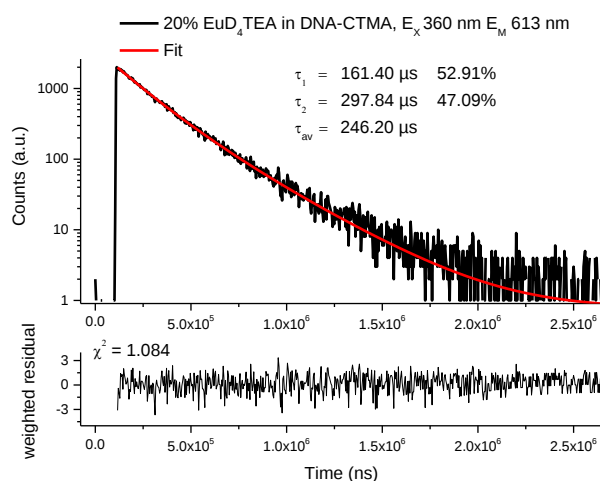


Figure S4. Time-resolved fluorescence decays and the relative fit of 20 % EuD₄TEA complex in the DNA-CTMA matrix. Emission wavelength 613 nm, excitation wavelength 360 nm.

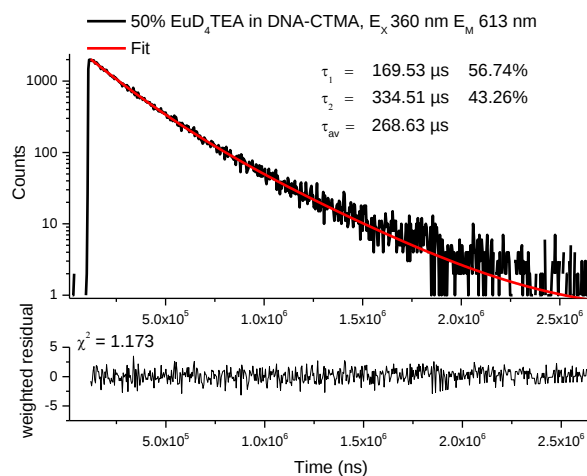


Figure S5. Time-resolved fluorescence decays and the relative fit of 50 % EuD₄TEA complex in the DNA-CTMA matrix. Emission wavelength 613 nm, excitation wavelength 360 nm.

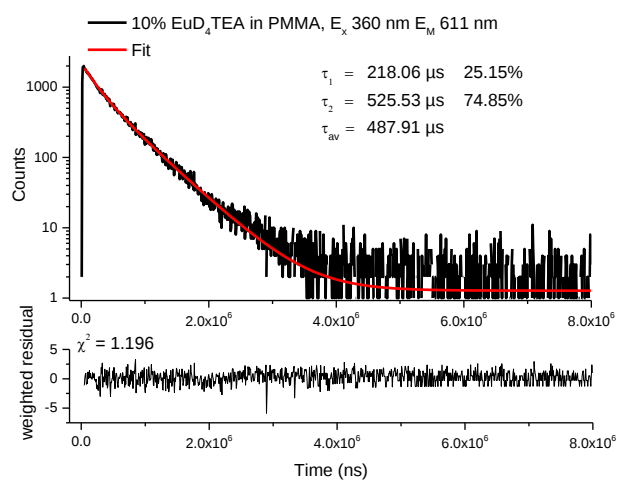


Figure S6. Time-resolved fluorescence decays and the relative fit of 10 % EuD₄TEA complex in the PMMA matrix. Emission wavelength 611 nm, excitation wavelength 360 nm.

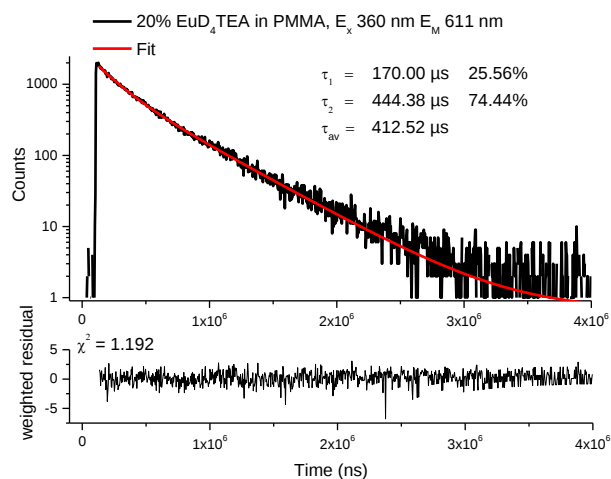


Figure S7. Time-resolved fluorescence decays and the relative fit of 20 % EuD₄TEA complex in the PMMA matrix. Emission wavelength 611 nm, excitation wavelength 360 nm.

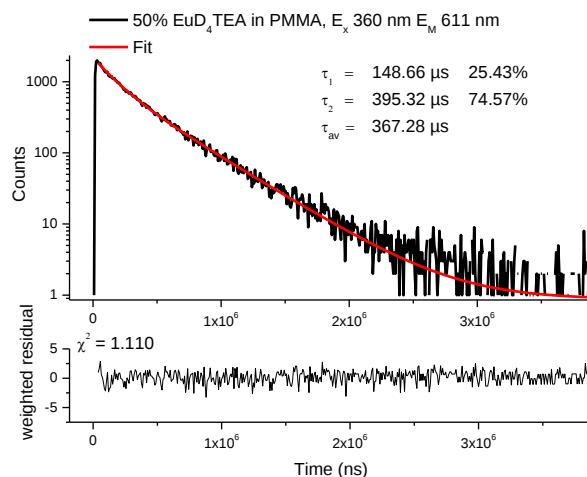


Figure S8. Time-resolved fluorescence decays and the relative fit of 50 % EuD₄TEA complex in the PMMA matrix. Emission wavelength 611 nm, excitation wavelength 360 nm.

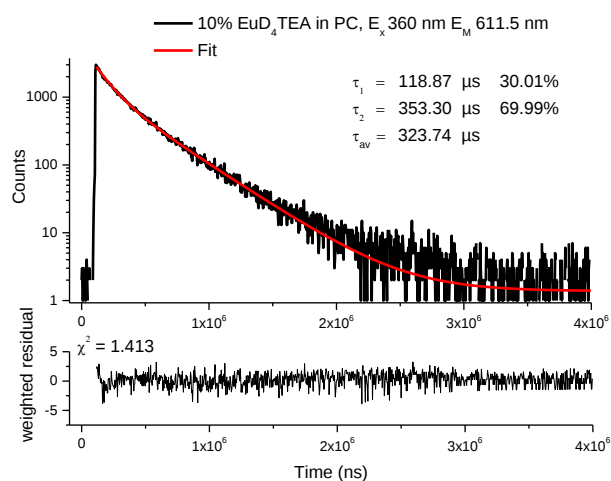


Figure S9. Time-resolved fluorescence decays and the relative fit of 10 % EuD₄TEA complex in the PC matrix. Emission wavelength 611.5 nm, excitation wavelength 360 nm.

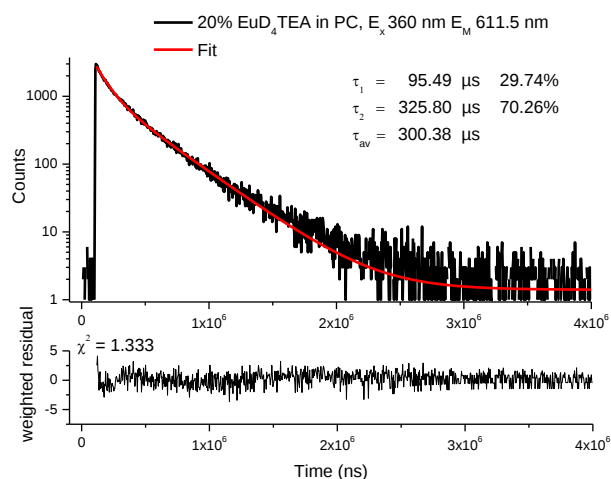


Figure S10. Time-resolved fluorescence decays and the relative fit of 20 % EuD₄TEA complex in the PC matrix. Emission wavelength 611.5 nm, excitation wavelength 360 nm.

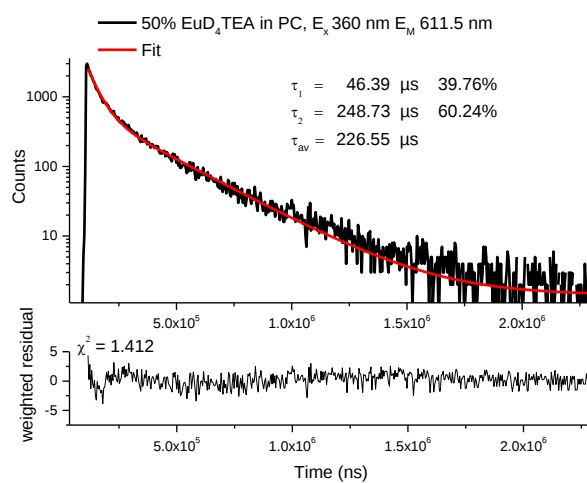


Figure S11. Time-resolved fluorescence decays and the relative fit of 50 % EuD₄TEA complex in the PC matrix. Emission wavelength 611.5 nm, excitation wavelength 360 nm.

Sample	Eu(III):Polymer (weight ratio of Eu(III))	Lifetime (μs)		Amplitude (%)		τ_{av} (μs)
		τ_1	τ_2	α_1	α_2	
PC/Eu(III)	1:2 (50 % wt)	46.39	248.73	39.76	60.24	226.55
	1:5 (20 % wt)	95.49	325.80	29.74	70.26	300.38
	1:10 (10 % wt)	118.87	353.30	30.01	69.99	323.74
PMMA/Eu(III)	1:2 (50 % wt)	148.66	395.32	25.43	74.57	367.28
	1:5 (20 % wt)	170.00	444.38	25.56	74.44	412.52
	1:10 (10 % wt)	218.06	525.53	25.15	74.85	487.91
DNA- CTMA/Eu(III)	1:2 (50 % wt)	169.53	334.51	56.74	43.26	268.63
	1:5 (20 % wt)	161.40	297.84	52.91	47.09	246.20
	1:10 (10 % wt)	180.33	430.01	65.74	34.26	318.68

Table S1. Lifetimes and amplitude of the two pre-exponential coefficients (α_1 and α_2) of the fitting exponential functions of the thin films of the EuD₄TEA complex at various concentrations in DNA-CTMA, PMMA and PC matrixes.

IV References

46. K. Suzuki, A. Kobayashi, S. Kaneko, K. Takehira, T. Yoshihara, H. Ishida, Y. Shiina, S. Oishic, S. Tobita, Reevaluation of absolute luminescence quantum yields of standard solutions using a spectrometer with an integrating sphere and a back-thinned CCD detector, *Phys. Chem. Chem. Phys.*, 2009, 11, 9850–9860. DOI: 10.1039/b912178a