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Carbostyryls monofluorinated in the 3, 5, or 6 positions were synthesised from olefinic precursors *via* a photochemical isomerisation-cyclisation route, and incorporated into octadentate cyclen triacetate ligands that formed luminescent complexes with Tb(III) and Eu(III). The photophysical properties of the emitters were strongly dependent on the position of the fluorination.

The luminescence of the trivalent lanthanide (Ln) ions is applied in diverse biological and industrial settings ranging from the monitoring of the components of living cells to the thermometric analysis of materials.^{1,2} Ln(III) luminescence is often sensitised by a light-harvesting antenna to avoid the need for direct excitation of the Laporte-forbidden 4f–4f transitions.³ Optimisation of energy transfer (EnT) to the Ln(III) and elimination of processes that quench the antenna and Ln(III) excited states are essential for bright emitters.

Photoinduced electron transfer (PeT) from the excited antenna to Ln(III) is feasible for several Lns,^{4,5} and for Eu(III) emission it can be an effective luminescence quenching process.⁶ PeT is suppressed when the antenna is less reducing. Antenna substitution with electron-withdrawing groups (e.g. with CF₃, Fig. 1)^{4,5} or protonation^{7,8} can increase the Eu(III) luminescence quantum yield, but may have unintended consequences on the antenna excited state energies.^{5,9,10} Ln sensitisation commonly takes place *via* the antenna singlet (S₁) and triplet excited states (T₁). Even subtle changes to the antenna may alter the S₁ and T₁ energies and EnT. In the previous examples both antenna trifluoromethylation^{4,5} and protonation proved detrimental to Tb(III) emission.⁸

Here, we have prepared three monofluorinated 7-aminocarbostyryl regioisomers. Electronegative fluorine was

expected to decrease PeT by making the antenna less reducing, a strategy that complements the use of C–F bonds to replace the more efficiently quenching C–H oscillators.¹¹ Fluorination has additional potential benefits. Fluorine is a hydrogen isostere conferring metabolic stability, H-bond acceptor ability, and altered lipophilicity on pharmaceuticals.¹² Diagnostic applications of fluorinated probes include multimodal¹³ and responsive¹⁴ systems. ¹⁹F-MRI is a promising low-background technique,¹⁵ and ¹⁸F is an attractive PET label.^{16,17}

Fluorinated carbostyryls were incorporated into do3a (1,4,7,10-tetraazacyclododecane-1,4,7-triacetate)-based octadentate ligands to enable comparison with previously reported structures.^{4,5} The Eu(III), Tb(III), and Gd(III) chelates of the ligands were characterised using ¹H NMR spectroscopy, cyclic voltammetry, and UV-vis absorption and steady-state and time-resolved emission spectroscopies. Our results show fluorination meaningfully impacts the antenna and Ln(III) photophysical properties, and substitution at a remote antenna position could even influence the excited state behaviour of the Ln(III).

Fluorinated antennae were synthesised as shown in Scheme 1 and Schemes S1–S6 (ESI[†]). The procedures were

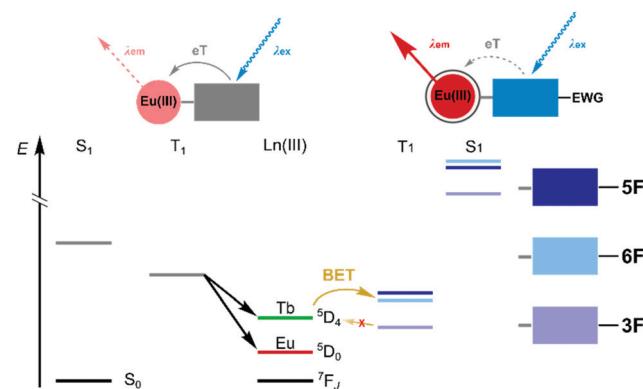
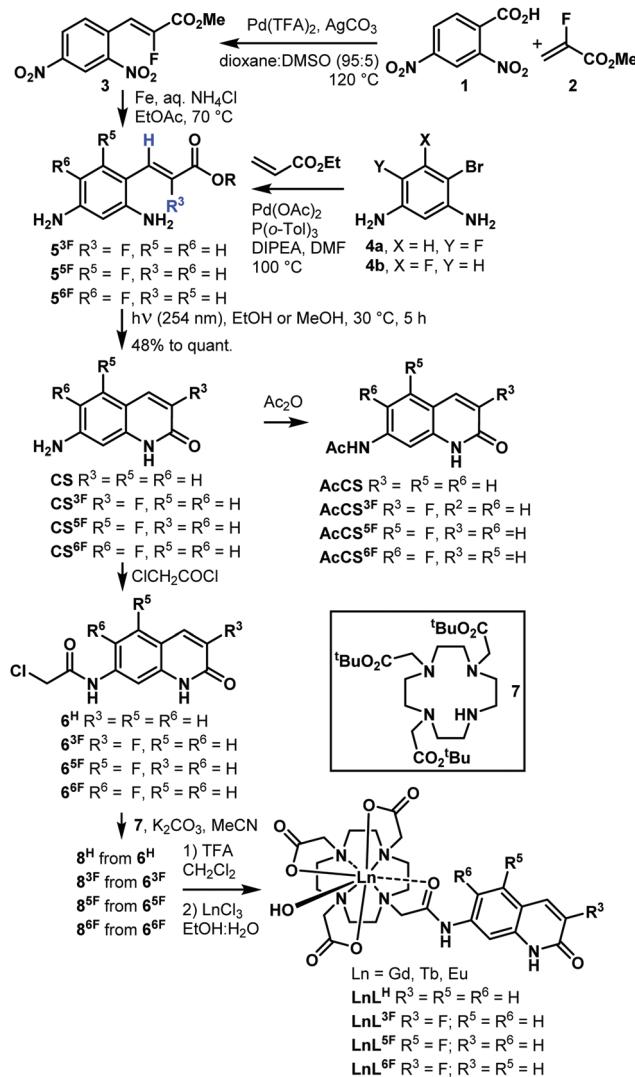


Fig. 1 Decreased PeT quenching of Eu(III) luminescence through antenna substitution with electron-withdrawing group(s) (EWG), and its effects on the S₁ and T₁ energies.

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Scheme 1 Preparation of CS^{F} , AcCS , AcCS^{F} , and LnL^{F} .

robust, scalable (e.g. 466 mg of CS^{6F} was obtained in one experiment), and reproducible. Olefins 5^{F} were prepared from commercially available starting materials as the *Z* isomers with excellent selectivity due to the steric clash between the ester group and the aromatic ring.¹⁸ The stereochemical assignment was based on the $^3J_{\text{HF}} = 33\text{--}38$ Hz and $^3J_{\text{HH}} = 15\text{--}16$ Hz coupling constants. The key photochemical olefin isomerisation-cyclisation was carried out by irradiating a 100 mM solution of 5 in MeOH or EtOH with 254 nm-UV light, giving CS^{3F} , CS^{5F} , and CS^{6F} in good to excellent yield. Regioisomer identities were confirmed by 1D and 2D NMR spectroscopy and single-crystal X-ray crystallography (Fig. S1–S6 and Tables S1–S3, ESI†). The analogous CS^{4F} could not be accessed *via* similar routes due to the instability of the intermediates (Schemes S3–S5, ESI†). CS^{F} was acetylated with Ac_2O or chloroacetyl chloride to yield reference compounds $\text{AcCS}/\text{AcCS}^{\text{F}}$, or the reactive antennae 6 , respectively. 6 were incorporated into LnL ($\text{Ln} = \text{Gd, Eu, Tb}$) using procedures previously developed for similar compounds. Synthetic details, compound characterisations, and the

attempted syntheses of CS^{4F} are given in the ESI.† Analytical data were fully consistent with the assigned structures.

Solution structures of EuL^{F} were studied by paramagnetic ^1H and ^{19}F NMR spectroscopy. In CD_3OD at r.t. the ^1H NMR spectra of EuL^{3F} , EuL^{5F} , EuL^{6F} , and EuL^{H} , were similar (Fig. S7–S10, ESI†). The major isomer had square antiprismatic geometry (4 peaks at >32 ppm). Trace amounts of the twisted square antiprismatic isomer were also present (signals at 12–16 ppm). ^{19}F NMR spectra supported this interpretation, showing a single peak at -133.8 , -118.8 , and -134.1 ppm for EuL^{3F} , EuL^{5F} , and EuL^{6F} , respectively (Fig. S11–S13, ESI†). These data are consistent with the ligands imposing similar geometries on the $\text{Ln}(\text{III})$ ions in solution in the ground state, and is similar to what has been observed for other do3a-complexes carrying carbostyryl antennae.⁶ This was expected as fluorine is small, and the fluorination sites are quite distant from the $\text{Ln}(\text{III})$.

The photophysical properties of CS and CS^{F} were recorded in acetonitrile due to their low aqueous solubility. The lowest-energy bands in the absorption spectra were assigned to $\pi\text{--}\pi^*$ transitions, and were located at 320–360 nm with $\lambda_{\text{max}} = 335$, 332, and 339 nm for CS^{3F} , CS^{5F} , and CS^{6F} , respectively (Fig. S18–S22, ESI†), non-fluorinated CS had $\lambda_{\text{max}} = 337$ nm. CS , CS^{3F} , CS^{5F} , and CS^{6F} excitation at λ_{max} resulted in fluorescence emission maxima at $\lambda_{\text{em}} = 384$, 400, 387, and 382 nm, respectively (Table 1 and Fig. S23–S27, ESI†). CS^{3F} had the highest fluorescence quantum yield, $\Phi_{\text{L}} = 56\%$. Fluorination in the 5-position had minimal effect on Φ_{L} compared to CS ($\Phi_{\text{L}} = 25$ and 27%, respectively), while substitution in the 6-position lowered Φ_{L} to 10%. CS^{F} fluorescence lifetimes (τ_{fl}) mirrored the observations made for Φ_{L} (Table 1). CS^{3F} had the longest τ_{fl} (2.84 ns), and CS^{6F} the shortest, $\tau_{\text{fl}} = 0.41$ ns. CS and CS^{5F} had very similar τ_{fl} , 1.15 and 1.09 ns, respectively (Table S5 and Fig. S49–S56, ESI†).

LnL absorption spectra were collected in aqueous solutions (0.01 M PIPES buffer, pH = 6.5). Absorption maxima were blue-shifted relative to the corresponding CS with $\lambda_{\text{max}} = 325$, 327, 337, and 330 nm for LnL^{3F} , LnL^{5F} , LnL^{6F} , and LnL^{H} , respectively (Fig. 2 and Fig. S28–S32, ESI†).

$\text{Gd}(\text{III})$ excited states are too high to accept energy from the antennae, therefore, GdL are useful for determining the

Table 1 Photophysical properties of CS , $\text{CS}^{\text{F},\text{a}}$ and $\text{GdL}^{\text{F},\text{b}}$

	λ_{max} (nm)	$\lambda_{\text{em}}^{\text{c}}$ (nm)	S_1 (cm^{-1})	T_1^{d} (cm^{-1})	$\Phi_{\text{L}}^{\text{e}}$ (%)	τ_{fl} (ns)
CS	337	384	—	—	27	1.15 (5)
CS^{3F}	335	400	—	—	56	2.84 (6)
CS^{5F}	332	387	—	—	25	1.09 (2)
CS^{6F}	339	382	—	—	10	0.41 (6)
GdL^{H}	330	369	28 700	22 500	7.6	0.34 (3)
GdL^{3F}	325	364	29 200	22 100	13	0.60 (5)
GdL^{5F}	327	367	28 900	22 400	6.1	0.44 (8)
GdL^{6F}	337	380	28 100	22 300	5.9	0.36 (4)

^a In acetonitrile at 10 μM concentration. ^b In aqueous PIPES buffer (10 mM), pH 6.5, at 10 μM complex concentrations. ^c $\lambda_{\text{ex}} = 332$ nm (CS^{3F}), 331 nm (CS^{5F}), 338 nm (CS^{6F}), 335 nm (GdL^{6F}), 327 nm (GdL^{5F}), 325 nm (GdL^{3F}). ^d Calculated from the 0–0 transitions of the Gd -complexes recorded at 77 K. ^e Relative to quinine sulfate ($\Phi = 0.59$) in H_2SO_4 (0.05 M).²³

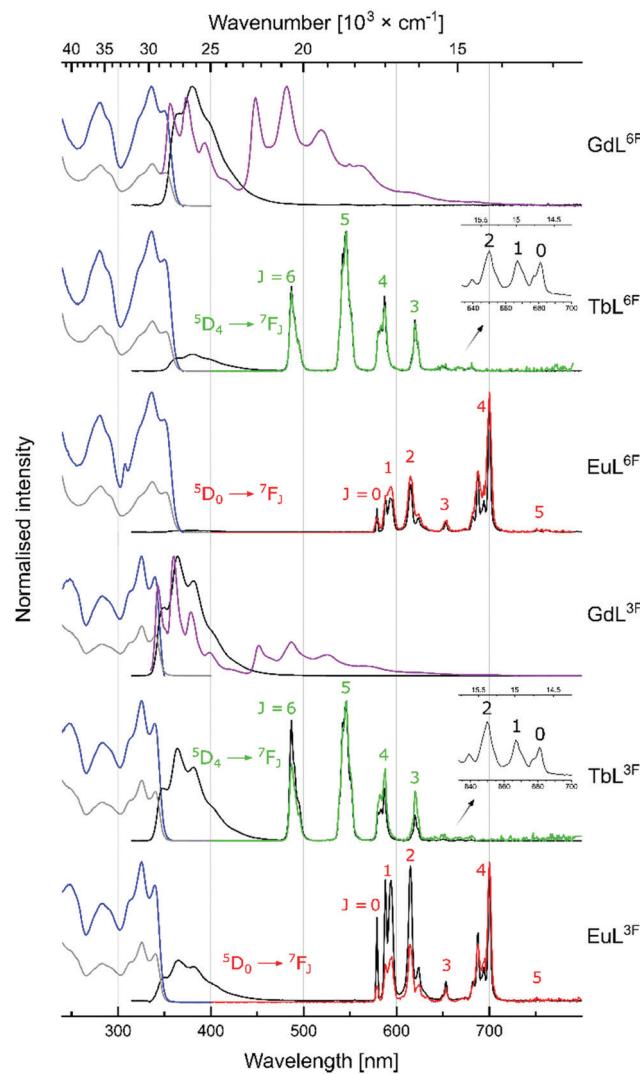


Fig. 2 Normalised absorption (grey, 298 K), excitation [blue, $\lambda_{\text{em}} = 380$ nm ($\text{GdL}^{6\text{F}}$), $\lambda_{\text{em}} = 364$ nm ($\text{GdL}^{3\text{F}}$), $\lambda_{\text{em}} = 615$ nm (Tb), $\lambda_{\text{em}} = 298$ K], steady-state emission at 298 K [black, $\lambda_{\text{ex}} = 335$ nm ($\text{LnL}^{6\text{F}}$), $\lambda_{\text{ex}} = 325$ nm ($\text{LnL}^{3\text{F}}$)], steady-state emission at 77 K [purple, $\lambda_{\text{ex}} = 335$ nm ($\text{LnL}^{6\text{F}}$), $\lambda_{\text{ex}} = 325$ nm ($\text{LnL}^{3\text{F}}$), 298 K] spectra of LnL^{F} .

antenna photophysical properties in LnL without interference from photo- or redox-active $\text{Ln}(\text{III})$. Carbostyryl excitation in GdL returned antenna fluorescence that was blue-shifted and less intense than that of the corresponding 7-aminocarbostyryl (Fig. S33–S36, ESI†). Φ_{L} was largest for $\text{GdL}^{3\text{F}}$ (13%) and smallest for $\text{GdL}^{6\text{F}}$ (5.9%), with $\Phi_{\text{L}}(\text{GdL}^{5\text{F}}) = 6.1\%$ and $\Phi_{\text{L}}(\text{GdL}^{\text{H}}) = 7.6\%$ in between. Steady state emission spectra were recorded at 77 K to determine the antenna T_1 (Fig. S45–S48, ESI†). Notably, fluorination in all three investigated positions lowered the antenna T_1 from $22\,500$ cm $^{-1}$ in GdL^{H} . $\text{GdL}^{3\text{F}}$ had the lowest energy T_1 ($22\,100$ cm $^{-1}$), and $\text{GdL}^{5\text{F}}$ had the highest, at only 300 cm $^{-1}$ higher energy. These are small but impactful differences. The $^5\text{D}_4$ emitting level of $\text{Tb}(\text{III})$ is located at $20\,400$ cm $^{-1}$, and the antenna T_1 must be at least ~ 2000 cm $^{-1}$ higher energy to avoid thermal back energy transfer (BET). Thus, $\text{TbL}^{3\text{F}}$ and possibly even $\text{TbL}^{6\text{F}}$ (but likely not $\text{TbL}^{5\text{F}}$) may be susceptible to BET. $\text{Tb}(\text{III})$ complexes that undergo BET are oxygen sensitive, and are useful for O_2 -sensing and cytotoxic singlet oxygen generation.^{19,20} T_1 are ~ 5000 cm $^{-1}$ higher than the emissive $^5\text{D}_0$ level of $\text{Eu}(\text{III})$, which is suitable for $\text{Eu}(\text{III})$ sensitization.²¹ T_1 in LnL^{F} are closer to the accepting $^5\text{D}_2$ $\text{Eu}(\text{III})$ level ($21\,500$ cm $^{-1}$) than in LnL^{H} , which may result in better energy transfer in the fluorinated complexes.^{21,22}

Excitation of TbL and EuL at λ_{max} yielded green and red $\text{Ln}(\text{III})$ luminescence, respectively (Fig. 2 and Fig. S37–S44, ESI† Table 2), with residual antenna fluorescence. TbL had slightly lower Φ_{L} than the analogous GdL likely due to some antenna S_1 -mediated EnT to $\text{Tb}(\text{III})$.⁶ EuL had drastically diminished Φ_{L} , which may be due to a combination of EnT from S_1 , and depopulation of S_1 by PeT. AcCS^{F} oxidation potentials (E_{ox}) were found by cyclic voltammetry as +1.73, +1.86, and +1.77 V (vs. NHE, for $\text{AcCS}^{3\text{F}}$, $\text{AcCS}^{5\text{F}}$, $\text{AcCS}^{6\text{F}}$, respectively); only 5-fluorination made antenna oxidation more difficult than in AcCS ($E_{\text{ox}} = +1.81$ V). PeT was calculated to be slightly less thermodynamically favoured in $\text{EuL}^{5\text{F}}$, and $\text{EuL}^{6\text{F}}$ than in EuL^{H} , and more favoured in $\text{EuL}^{3\text{F}}$ ($\Delta G(\text{PeT}) = -1.01$, -1.14 , -0.98 , and -0.97 eV, for EuL^{H} , $\text{EuL}^{3\text{F}}$, $\text{EuL}^{5\text{F}}$, and $\text{EuL}^{6\text{F}}$, respectively (see ESI† for details)). Thus, the effects of fluorination on the antenna S_1 , T_1 and E_{ox} , and in turn on $\Delta G(\text{PeT})$ can be difficult to predict.

Table 2 Photophysical properties of LnL^{F} ($\text{Ln} = \text{Eu}, \text{Tb}$),^a and τ_{rad} , $\Phi_{\text{Ln}}^{\text{Ln}}$, and η_{sens} $\text{EuL}^{\text{F}}\text{b}$

	$\Phi_{\text{L}}^{\text{cd}}\text{ (}\%$	τ_{fl} (ns)	$\Phi_{\text{Ln}}^{\text{c}}$ (%)	τ_{rad} (ms)	$\Phi_{\text{Ln}}^{\text{Ln}}$ (%)	η_{sens} (%)
TbL^{H}	5.1 (67%)	0.21(4)	22.5	—	—	—
$\text{TbL}^{3\text{F}}$	8.1 (63%)	0.39(2)	5.6	—	—	—
$\text{TbL}^{5\text{F}}$	4.6 (75%)	0.36(3)	21.7	—	—	—
$\text{TbL}^{6\text{F}}$	4.6 (78%)	0.25(4), 2.40(3) ^e	16.7	—	—	—
EuL^{H}	0.261 (3.4%)	— ^f	4.34	5.18 ^g , 4.73 ^h	11.9 ^g , 13.1 ^h	36.2 ^g
$\text{EuL}^{3\text{F}}$	0.680 (5.3%)	0.93(6), 0.42(5) ^e	1.09	9.25 ^g , 5.10 ^h	6.7 ^g , 12.3 ^h	16.1 ^g
$\text{EuL}^{5\text{F}}$	0.814 (13%)	0.47(6), 1.76(5) ^e	5.05	5.25 ^g , 5.11 ^h	11.5 ^g , 11.8 ^h	43.4 ^g
$\text{EuL}^{6\text{F}}$	0.207 (3.5%)	0.20(1), 2.85(5) ^e	5.10	5.28 ^g , 5.19 ^h	11.6 ^g , 11.8 ^h	43.8 ^g

^a $[\text{LnL}] = 10 \mu\text{M}$ in 10 mM PIPES buffered H_2O , pH 6.5. ^b Determined using the method in ref. 26. $I_{\text{tot}}/I_{\text{MD}}$: integral ratio of total Eu-centred corrected emission spectrum (570–800 nm) and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ band (582–603 nm), $A_{\text{MD},0} = 14.65 \text{ s}^{-1}$, $n = 1.333$ (refractive index),²⁷ $\tau_{\text{obs}} = \tau_{\text{H}_2\text{O}}$.

^c Relative to quinine sulfate ($\Phi = 0.59$) in H_2SO_4 (0.05 M).²³ ^d In parentheses: compared to GdL analogue. ^e Biexponential fit better based on χ^2 .

^f Too short to measure. ^g Calculated from the steady-state emission spectra. ^h Calculated from the time-resolved emission spectra.

The $\text{Ln}(\text{III})$ luminescence lifetimes ($\tau_{\text{H}_2\text{O}}$) were measured by time-resolved emission spectroscopy. The decays were monoexponential. $\tau_{\text{H}_2\text{O}}$ values varied for $\text{Ln} = \text{Tb}$ but were almost identical for all EuL (~ 0.61 ms) (Table S4, ESI†). The number of $\text{Ln}(\text{III})$ -bound water molecules (q) were $q = 1$ for EuL . Deviations for TbL from $q = 1$ could be due to BET, which makes this method inapplicable,^{24,25} or the result of the typical error of $q \pm 0.5$.

$\text{TbL}^{5\text{F}}$ and TbL^{H} had the highest Tb-centred luminescence quantum yields ($\Phi_{\text{Ln}} = 21.7\%$ and 22.5% , respectively, values identical within experimental error). The low Φ_{Ln} of $\text{TbL}^{3\text{F}}$ is presumably the result of BET. $\text{EuL}^{5\text{F}}$ and $\text{EuL}^{6\text{F}}$ had $\Phi_{\text{Ln}} \sim 5\%$, which is higher than most $\text{Eu}(\text{III})$ complexes with similar structures, *i.e.* uncharged do3a-based emitters with secondary amide-linked carbostyryl antenna, including EuL^{H} ($\Phi_{\text{Ln}} = 4.34\%$). $\text{EuL}^{3\text{F}}$, however, had low $\Phi_{\text{Ln}} = 1.09\%$. Unlike $\text{TbL}^{3\text{F}}$, $\text{EuL}^{3\text{F}}$ does not suffer from BET, therefore, an alternative explanation for the poor performance of this emitter was necessary.

Φ_{Ln} is the product of the intrinsic quantum yield of the $\text{Ln}(\text{III})$ ($\phi_{\text{Ln}}^{\text{Ln}}$) and the $\text{Ln}(\text{III})$ sensitisation efficiency (η_{sens} , eqn (1)), *i.e.* the efficiency of $\text{Ln}(\text{III})$ excited state population. For $\text{Eu}(\text{III})$ $\phi_{\text{Ln}}^{\text{Ln}}$ can be determined from the corrected emission spectrum.²⁶

$$\phi_{\text{Ln}} = \eta_{\text{sens}} \cdot \phi_{\text{Ln}}^{\text{Ln}} = \eta_{\text{sens}} \cdot \frac{\tau_{\text{obs}}}{\tau_{\text{rad}}} \quad (1)$$

In $\text{EuL}^{5\text{F}}$ and $\text{EuL}^{6\text{F}}$ η_{sens} is increased compared to EuL^{H} , presumably due to a combination of the small adjustments in spectral overlap and PeT quenching. $\text{EuL}^{3\text{F}}$ had markedly lower η_{sens} and $\phi_{\text{Ln}}^{\text{Ln}}$ than the other EuL (Table 2). The steady-state and time-resolved $\text{EuL}^{3\text{F}}$ emission spectra have different shapes. $\text{Eu}(\text{III})$ spectra are sensitive to coordination environment, and these differences indicate the presence of several emissive species.²¹ The signal of the slow-decaying component dominating the time-resolved spectrum resembles the $\text{EuL}^{5\text{F}}/\text{EuL}^{6\text{F}}/\text{EuL}^{\text{H}}$ spectra. Contribution from the fast-decaying species modifies the steady-state $\text{EuL}^{3\text{F}}$ spectrum. If τ_{obs} is assumed unchanged, the steady-state spectral shape yields a lower overall $\phi_{\text{Ln}}^{\text{Ln}}$ (Table 2). The spectrum of $\text{TbL}^{3\text{F}}$ is similarly time-dependent, but not those of $\text{Eu/TbL}^{5\text{F}}$ and $\text{Eu/TbL}^{6\text{F}}$. The reasons for the diminished η_{sens} of $\text{EuL}^{3\text{F}}$ are unclear. PeT is more favoured in $\text{EuL}^{3\text{F}}$ than in $\text{EuL}^{5\text{F}}$ and $\text{EuL}^{6\text{F}}$, and EuL^{F} have much lower Φ_{L} than the corresponding GdL^{F} , which is consistent with PeT quenching. The τ_{fl} of EuL^{F} and GdL^{F} , however, cannot be compared directly. The biexponential decay of the EuL^{F} antenna fluorescence suggested the presence of additional emitters to those seen in GdL^{F} . Further work is therefore needed to understand the effect of fluorination on EnT and PeT.

In conclusion, monofluorinated 7-aminocarbostyryls, obtained *via* a photochemical cyclisation, were competent sensitizers of $\text{Eu}(\text{III})$ and $\text{Tb}(\text{III})$ emission. The position of the fluorine had a dramatic impact on the antenna and $\text{Ln}(\text{III})$ photophysical properties, rendering the emission oxygen-sensitive ($\text{TbL}^{3\text{F}}$, $\text{TbL}^{4\text{F}}$), and increasing ($\text{EuL}^{5\text{F}}$, $\text{EuL}^{6\text{F}}$), or decreasing Φ_{Ln} , ($\text{TbL}^{3\text{F}}$, $\text{TbL}^{6\text{F}}$, $\text{EuL}^{3\text{F}}$) compared to non-fluorinated LnL^{H} . 5-Fluorination improved $\text{Eu}(\text{III})$ emission without negatively impacting $\text{Tb}(\text{III})$ luminescence. Remote fluorination influenced the excited-state behaviour of $\text{LnL}^{3\text{F}}$. Work towards the 4-fluorinated isomer, and ligands containing other EWGs than fluorine is ongoing.

D. K. did all experiments except the crystallographic analysis, which was done by A. O. K. E. B. designed the project, secured funding, and supervised the work. All authors contributed to data analysis and manuscript writing.

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Conflicts of interest

There are no conflicts to declare.

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