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Supporting Information

Chiral Supramolecular Polymerization Leading to Eye Differentiable Circular Polarization in Luminescence

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Table of Contents

Experimental Section

Materials and Methods

All the chemical reagents were commercially available and used as received. The complexes were synthesized following procedures reported in literature.[1] Solvents such as chloroform and hexane used were of spectroscopic grade. Mass spectra were measured using a Bruker Autoflex II MALDI-TOF mass spectrometer. Absorption and emission spectra were measured using a JASCO V-670 spectrophotometer and using a JASCO FP-6500 spectrofluorometer, respectively. The emission quantum yields were determined by using a calibrated integrating sphere system. The emission lifetime was measured on a Hamamatsu, C4334 system. CD and CPL spectra were measured using a JASCO J-725 spectropolarimeter and a homemade CPL spectroscopy system (Figure S5), respectively. The CPL dissymmetry, $g_{\mathrm{lum}} = 2(I_L - I_R)/(I_L + I_R)$ of $M^+[Eu((+)\text{-hfbc})_4]^-$ in monomer and aggregated states were carefully determined using the experimental setup designed based on fluorescence spectrofluorometer (JASCO FP-6500) with the rotatable $\lambda/4$ filter and the linearly polarized plate (see Figure S6–S8 for details).

Preparation of Helical Aggregates and TEM Measurements.

Four pairs of enantiomers of europium complexes $M^+[Eu((+)\text{-hfbc})_4]^-$ (M = Na, K, Rb, Cs) were prepared and purified according to the reported procedure.[1] The complexes were carefully purified by recrystallization in acetonitrile. The helical aggregates were prepared by adding chloroform solution of the complexes to hexane. The stock solution of the complexes in chloroform was warmed gently for complete solubilisation. 1 mM solution of complexes in chloroform (200 µL) was added dropwise to a 4.8 mL stirring hexane in a sample vial. The addition was completed in 5 minutes and the solution in hexane was allowed to stir for 10-15 minutes before drop casting on to the TEM grid. Unstained specimens for TEM were prepared by dropping 100 µl the solution onto carbon-coated copper grid placed on a filter paper. After drying the samples overnight, TEM imaging was performed using a JEOL JEM-2200FS operating at 200 kV with an electron energy filter.

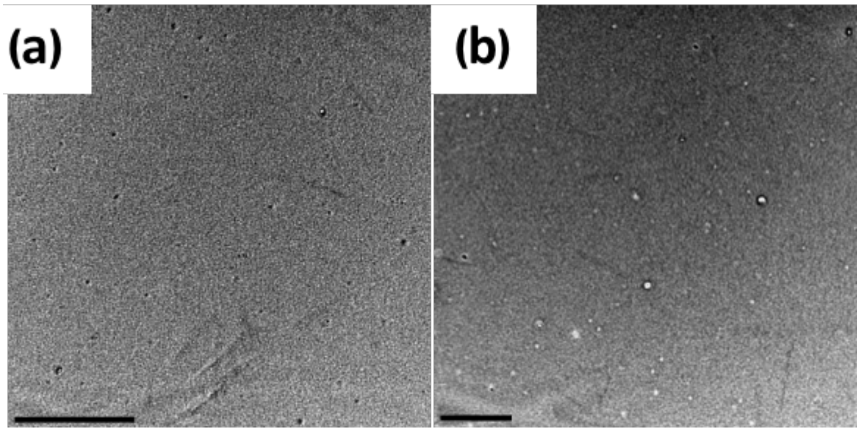

Fig. S1 TEM images of Cs$^+$[Eu((+)-hfbc)$_4$]$^-$ in (a) chloroform and (b) ethanol at a concentration of 4.0 × 10^{-5} M.

Note: The absence of any aggregates suggests that the complexes remain in the monomeric state in pure chloroform/ethanol and self-assembles in hexane.

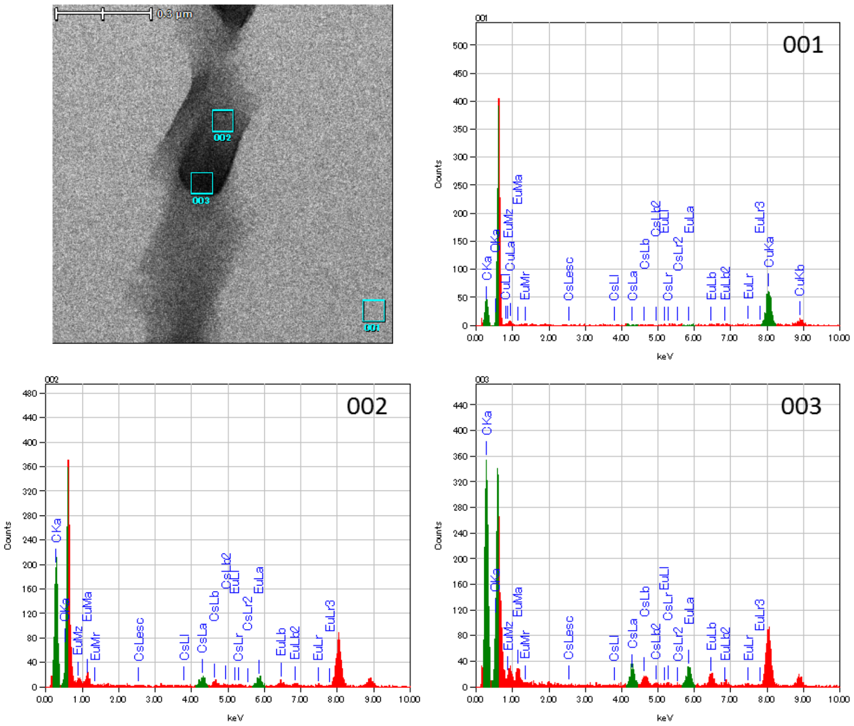

Fig. S2 High resolution TEM image and the EDX from the surface of the aggregate (002 and 003) as well as background (001) of Cs$^+$[Eu((+)-hfbc)$_4$]$^-$ formed in a mixture of (1:24) of chloroform:hexane.

Note: The presence of Eu and Cs on the surface of the aggregates (002 and 003) is a clear indication of the fact that the aggregates are composed of the complexes and not any dissociated products.

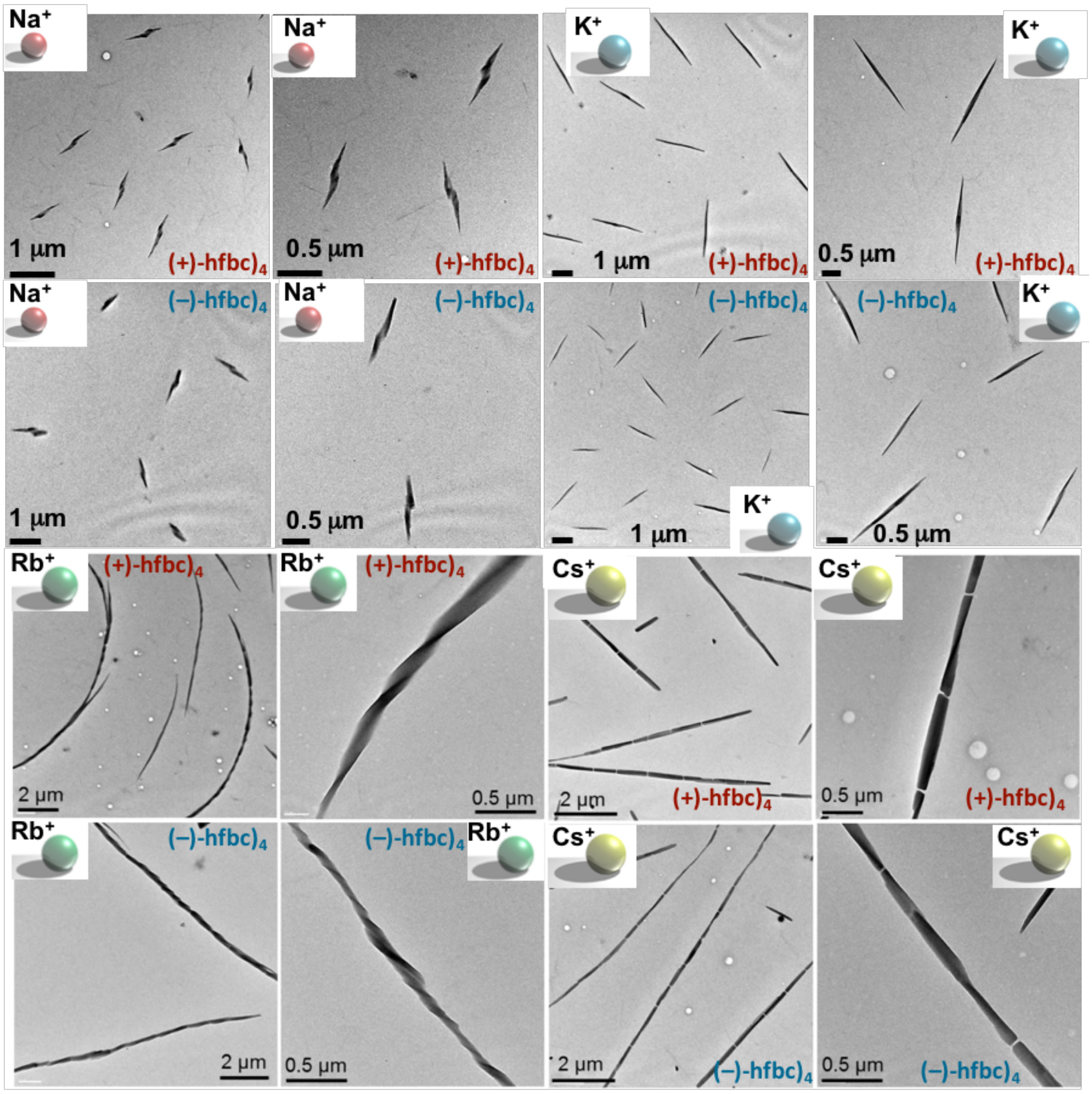

Fig. S3 TEM images of M$^+$[Eu((+)-hfbc)$_4$]$^-$ and M$^+$[Eu((–)-hfbc)$_4$]$^-$ (M = Na, K, Rb, Cs) in a mixture (1:24) of chloroform:hexane (concentration = 4.0 x 10^{-5} M).

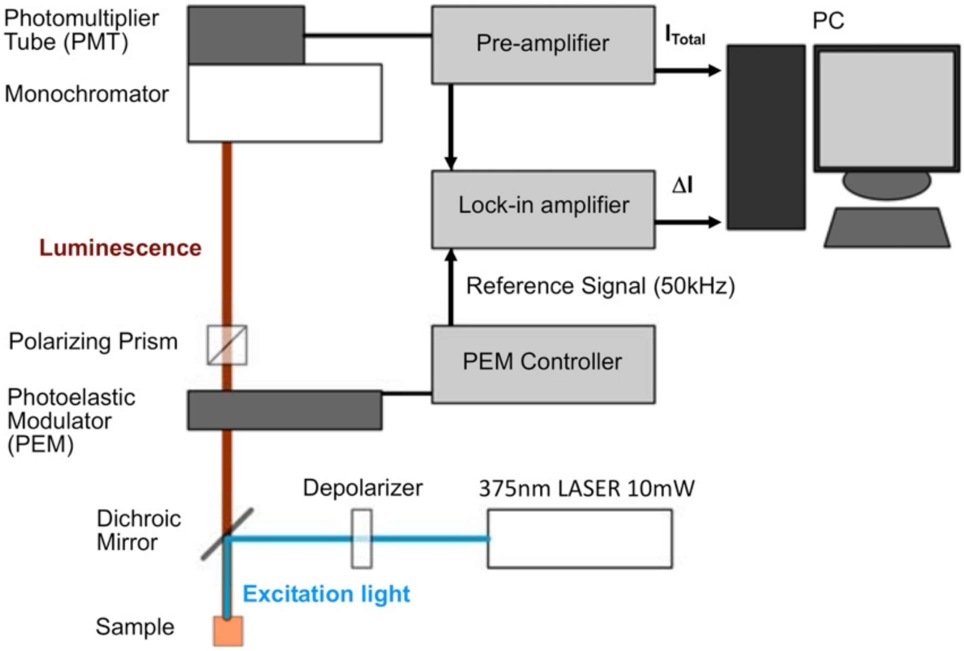

Fig. S4 Schematic diagram of our CPL measurement system in which an excitation laser of 375 nm in wavelength is irradiated to the sample from the same-side to the detection in the epi illumination configuration. The retardation of the emitted light was controlled by a photo-elastic modulator (Hinds, PEM-90) that is modulated with the frequency of 50kHz. The circularly polarized component was converted to the linearly polarized light and detected by a photomultiplier tube (Hamamatsu, H7732-10) after passing through the linearly polarized cubic prism (200,000:1) for analyzing circularly polarized luminescence (CPL) signal. In order to maintain a circularly polarized component in the emission, the dichroic filter was precisely settled to be 45^{o} against the optical path. The AC component of the PMT output with frequency of 50kHz was analyzed by a lock-in amplifier (EG&G, Model 7265), which can be modulated by the reference frequency signal from the PEM. A PC system controls the monochromator and the PEM for the appropriate detection wavelength. The calibration of the EI-CPL was performed by reference to obtained data from a CPL spectrometer (JASCO, CPL-200). A description of other components in the measurement system as follows; depolarizer (SIGUMA KOKI CO., LTD., DEQ-S2), dichroic mirror (Chroma Technology Corp., Z375RDC), polarizing prism (Edmund Optics Japan Ltd., 47045-K), monochromator (SHIMADZU CORPORATION, SPG-120S), pre-amplifier (Stanford Research Systems, SR570).

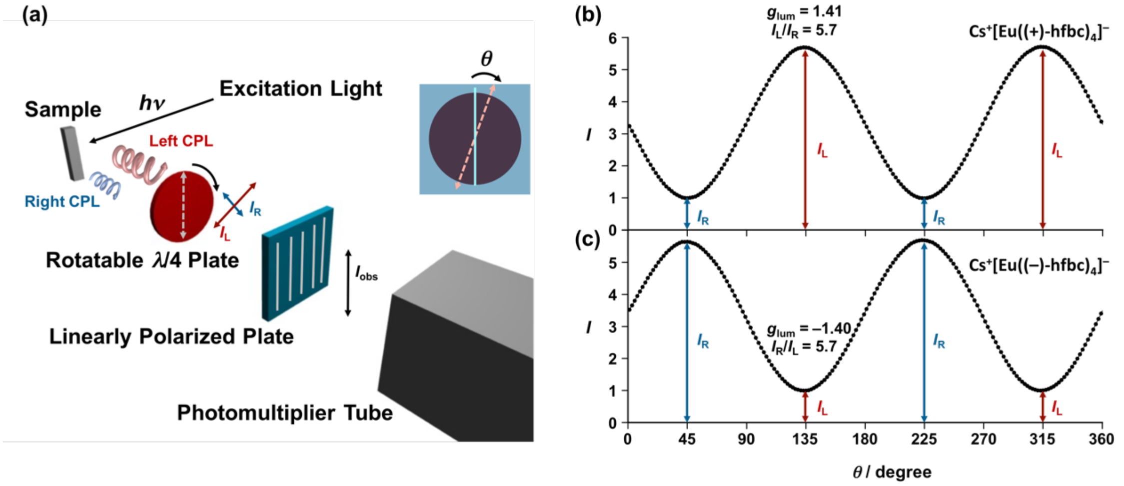

Figure S5. (a) Schematic illustration of experimental setup for determination of g_{lum} values of $M^+[Eu((+)\text{-hfbc})_4]^-$ in solution and aggregated states. The experimental setup was designed based on fluorescence spectrofluorometer (JASCO FP-6500) with the rotatable λ/4 filter and the linearly polarized plate. The circularly polarized component (left- and right-CPL) from the sample was converted to the linearly polarized light (I_{L} and I_{R}, respectively) after passing through the rotatable λ/4 filter. Then, the linearly polarized light (I_{L} and I_{R}) was detected by a photomultiplier tube after passing through the linearly polarized plate for analyzing circularly polarized luminescence (CPL) signal. The observed emission intensity (I_{obs}) periodically increases and decreases depending on the angle (θ) between the rotatable λ/4 filter and the linearly polarized plate. The intensity obtained at the angle θ = 45, 225 and 135, 315 degrees corresponds to right- and left-CPL (I_{R} and I_{L}, respectively). Periodicity is at every 90 degrees as there is no the linearly polarized component from the sample. The CPL dissymmetry, $g_{\mathrm{lum}} = 2(I_{\mathrm{L}} - I_{\mathrm{R}})/(I_{\mathrm{L}} + I_{\mathrm{R}})$, were evaluated from 5 sets of measurements. (b,c) The complete mirror images were obtained between the enantiomers ($Cs^+[Eu((+)\text{-hfbc})_4]^-$ and $Cs^+[Eu((–)\text{-hfbc})_4]^-$): plots of emission intensity of (b) $Cs^+[Eu((+)\text{-hfbc})_4]^-$ and (c) $Cs^+[Eu((–)\text{-hfbc})_4]^-$ (conc. = 4.0 x 10^{-5} M) at λ = 595 nm vs the angle (θ) between the rotatable λ/4 filter and the linearly polarized plate in chloroform. The intensity was normalized by the minimum value at (b) θ = 45 degrees and (c) = 135 degrees. Excitation wavelength: λ_{ex} = 371 nm. The determined g_{lum} value (1.41) of $Cs^+[Eu((+)\text{-hfbc})_4]^-$ is close to the literature value (g_{lum} = 1.38).[2]

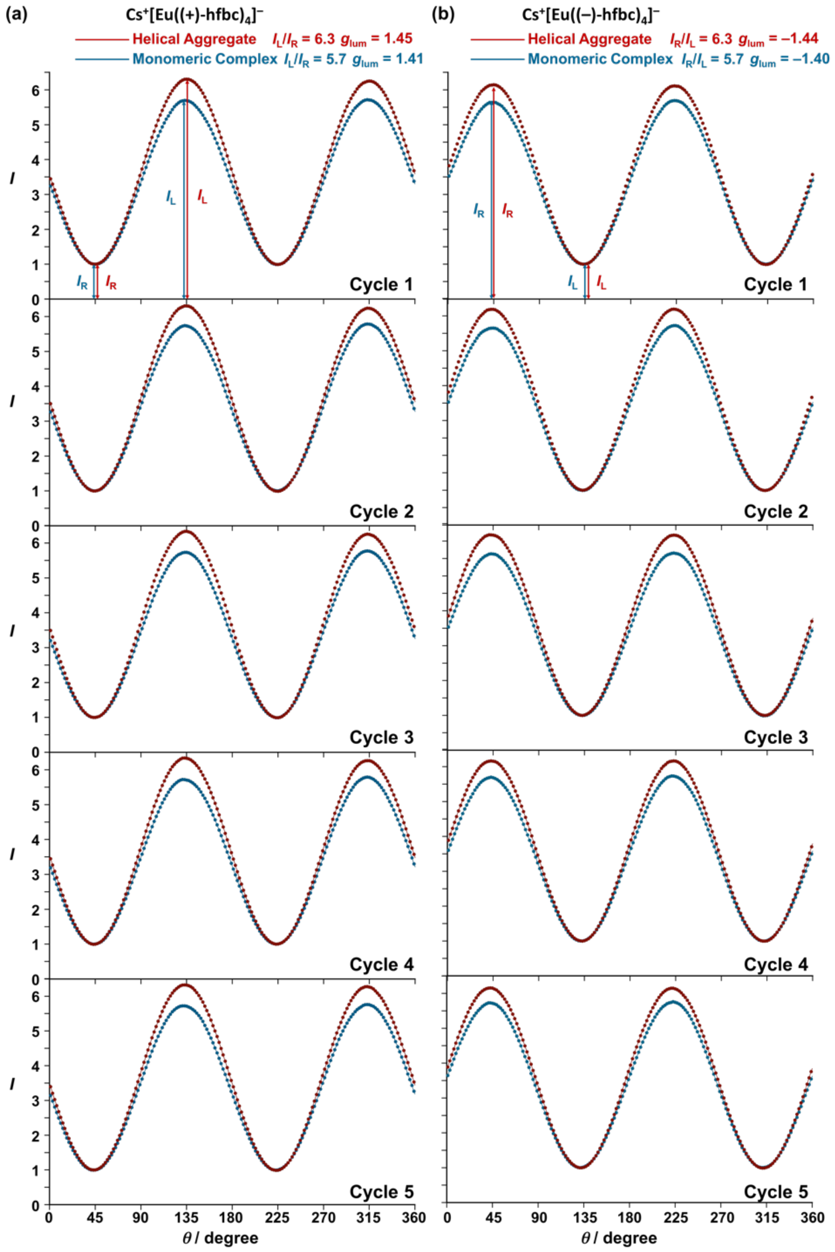

Figure S6. Plots of emission intensity of (a) $Cs^+[Eu((+)-hfbc)_4]^-$ and (b) $Cs^+[Eu((–)-hfbc)_4]^-$ (conc. = 4.0 x 10^{-5} M) as monomeric complexes (blue dots) in chloroform and as helical aggregates (red dots) in a mixture (1:24) of chloroform:hexane at λ = 595 nm vs the angle (θ) between the rotatable $\lambda/4$ filter and the linearly polarized plate. The intensity was normalized by the minimum value at (a) θ = 45 degrees and (b) = 135 degrees. Excitation wavelength: λ_{ex} = 371 nm. The CPL dissymmetry, $g_{lum} = 2(I_L - I_R)/(I_L + I_R)$, were evaluated from 5 sets of measurements.

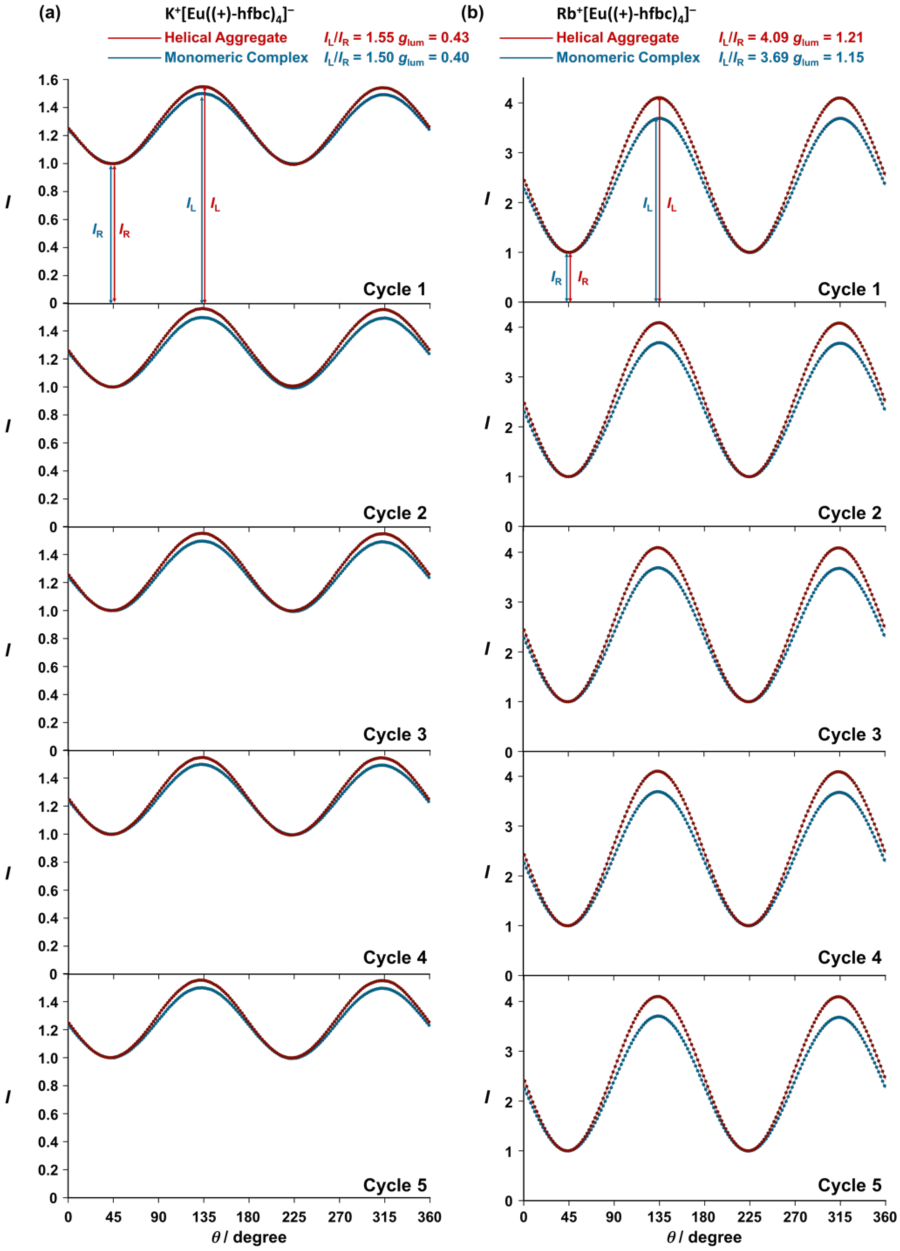

Figure S7. Plots of emission intensity of (a) $K^+[Eu((+)\text{-hfbc})_4]^-$ and (b) $Rb^+[Eu((+)\text{-hfbc})_4]^-$ (conc. = 4.0 x 10^{-5} M) as monomeric complexes (blue dots) in chloroform and as helical aggregates (red dots) in a mixture (1:24) of chloroform:hexane at $\lambda = 595$ nm vs the angle (θ) between the rotatable $\lambda/4$ filter and the linearly polarized plate. The intensity was normalized by the minimum value at $\theta = 45$ degrees. Excitation wavelength: $\lambda_{ex} = 371$ nm. The CPL dissymmetry, $g_{lum} = 2(I_L - I_R)/(I_L + I_R)$, were evaluated from 5 sets of measurements.

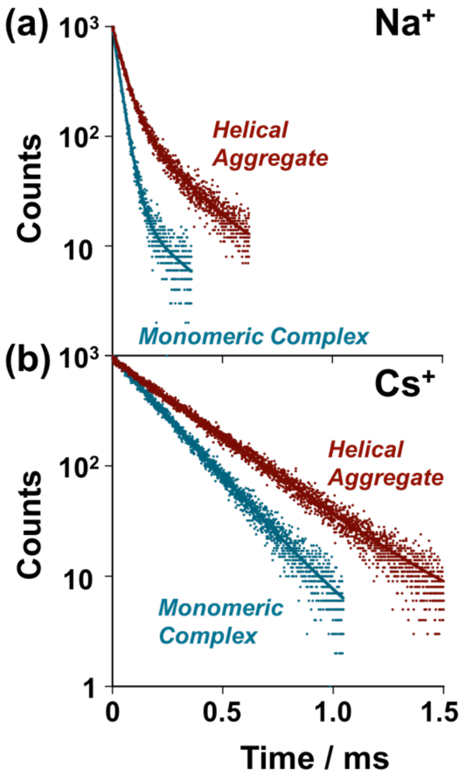

Figure S8. Emission decay curves of (a) $Na^+[Eu((+)\text{-hfbc})_4]^-$ and (b) $Cs^+[Eu((+)\text{-hfbc})_4]^-$ at $\lambda = 614$ nm in chloroform (blue dots) and in a mixture (1:24) of chloroform:hexane (red dots), and those recorded after 24 hours (green dots).

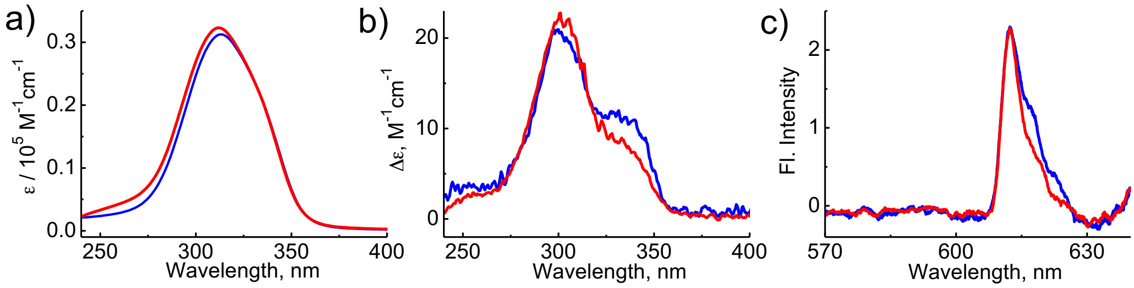

Figure S9. (a) Absorption, (b) CD and (c) emission spectra of the [Eu((+)-hfbc)$_3$] in ethanol (blue lines) and in a mixture (1:24) of ethanol:hexane (red lines) (conc. = 4.0 x 10^{-5} M).

Note: The weak CD, fluorescence and CPL (could not be measured) spectral features clearly suggests that the coexisting of Eu((+)-hfbc)$_3$ will decrease the overall g_{CD} and g_{lum} values of the complexes.

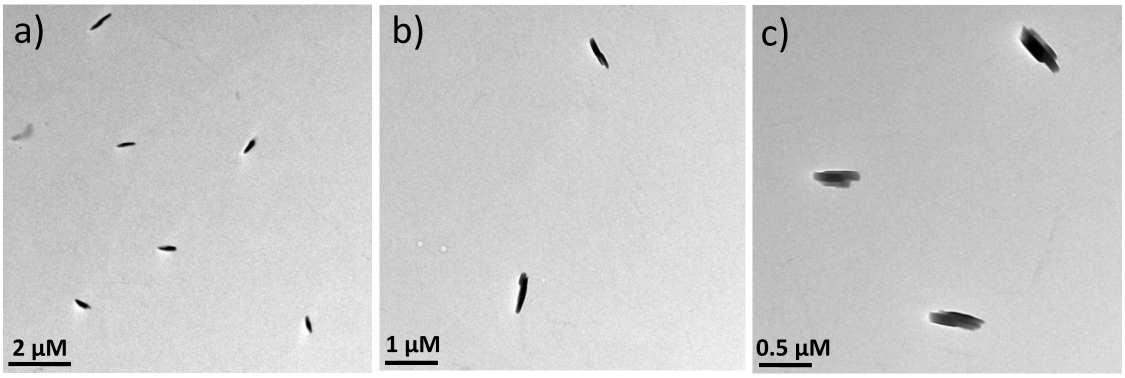

Figure S10. TEM images of Eu((+)-hfbc)$_3$ in a mixture (1:24) of chloroform:hexane (conc. = 4 x 0^{-5} M).

Note: Small ill-defined nanostructures formed from Eu((+)-hfbc)$_3$ were found only in low concentration at certain parts of the grid. These results clearly illustrate the role of metal ion in inducing the growth of helical aggregates. This further emphasizes the fact that the ionic and dipolar interactions involving the alkali metals (M^+), europium(III) and the fluorine atoms in $M^+[Eu((+)\text{-}hfbc)_4]^-$ is responsible for the one dimensional growth of helical aggregates in hexane.

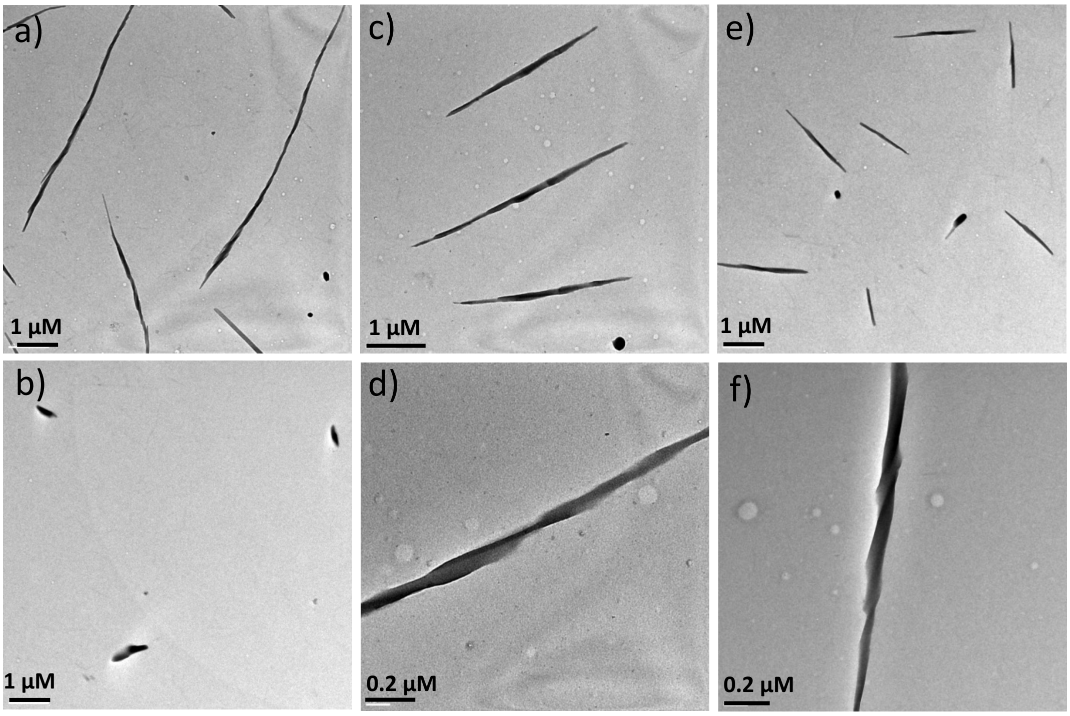

Figure S11. TEM images of (a) $Cs^{+}[Eu((+)\text{-}hfbc)_4]^{-}$ and (b) $Eu((+)\text{-}hfbc)_3$ in a mixture (1:24) of chloroform:hexane (concentration = 4 x 0^{-5} M). TEM images of $Cs^{+}[Eu((+)\text{-}hfbc)_4]^{-}$ in the presence of $Eu((+)\text{-}hfbc)_3$ in (c, d) 2:1 and (e,f) 1:1 ratio, in a mixture (1:24) of chloroform:hexane.

Note: Chloroform solutions of $Cs^{+}[Eu((+)\text{-}hfbc)_4]^{-}$ *and* $Eu((+)\text{-}hfbc)_3$ *were mixed in different ratios and the mixture was added to stirring hexane solution (concentration maintained at 4 x* 10^{-5} *M) to obtain helical structures with varying length dependent on the concentration of* $Eu((+)\text{-}hfbc)_3$*. The length as well as population of the aggregates decreases with increasing proportion of* $Eu((+)\text{-}hfbc)_3$*. The helicity of the fibers (clockwise twist) is maintained in all the cases (d,f). This experiment clearly demonstrates the growth inhibition effect of* $Eu((+)\text{-}hfbc)_3$*.*

References

1 D. Shirotani, T. Suzuki and S. Kaizaki, *Inorg. Chem.*, 2006, **45**, 6111.

2 J. L. Lunkley, D. Shirotani, K. Yamanari, S. Kaizaki and G. Muller, *J. Am. Chem. Soc.*, 2008, **130**, 13814.