Supplementary Material (ESI) for Journal of Materials Chemistry

Optically controllable polarized luminescence from azopolymer film doped with lanthanide complex

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Electronic Supplementary Information (ESI)

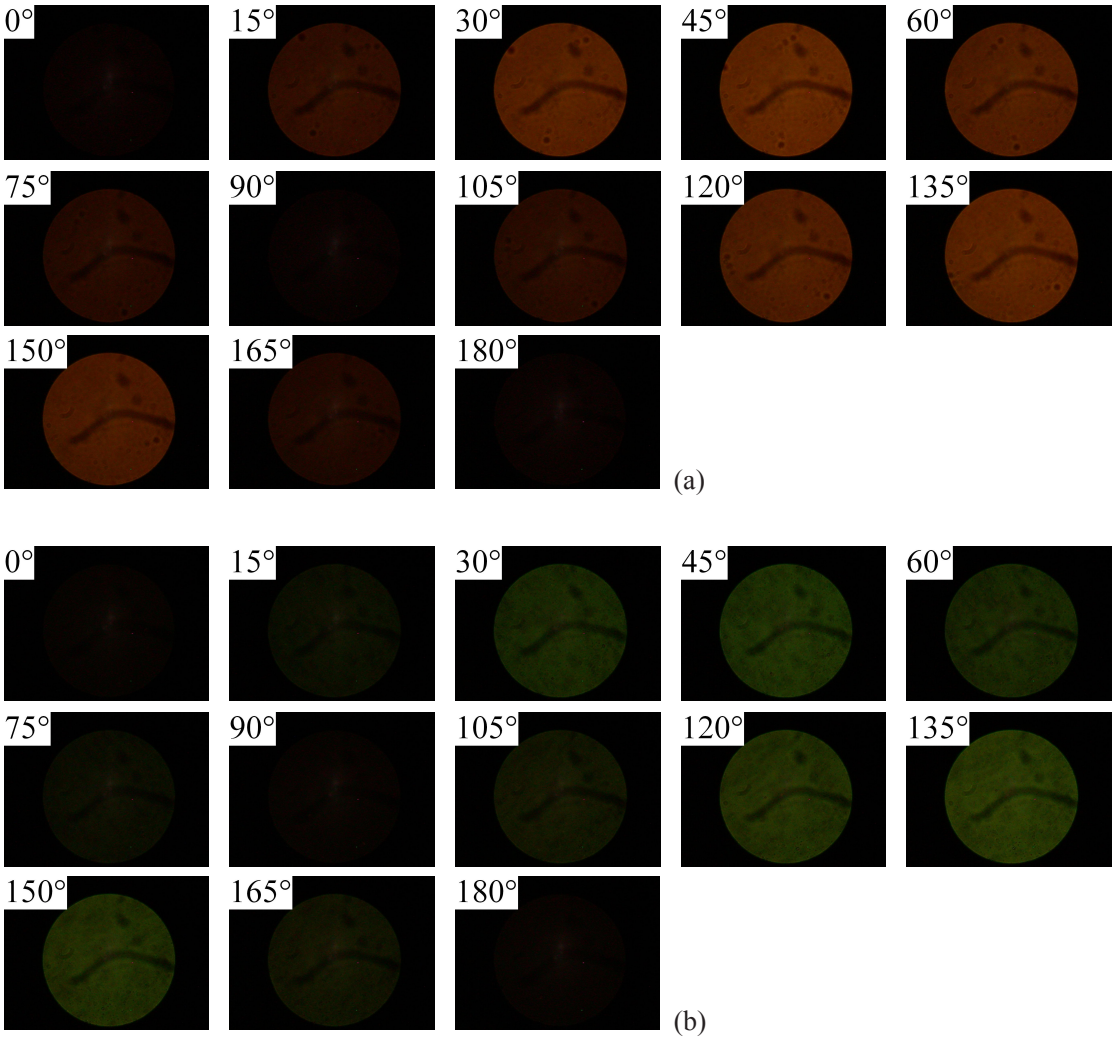

Figure S1 The POM images of (a) $DACENO_2/Eu(TTA)_3Phen$ film and (b) $DACEOCH_3/Eu(TTA)_3Phen$ film after photo-induced orientation with different angles to the polarizer. The black bands and dots in the bright field are something on the ocular but not something on the samples.

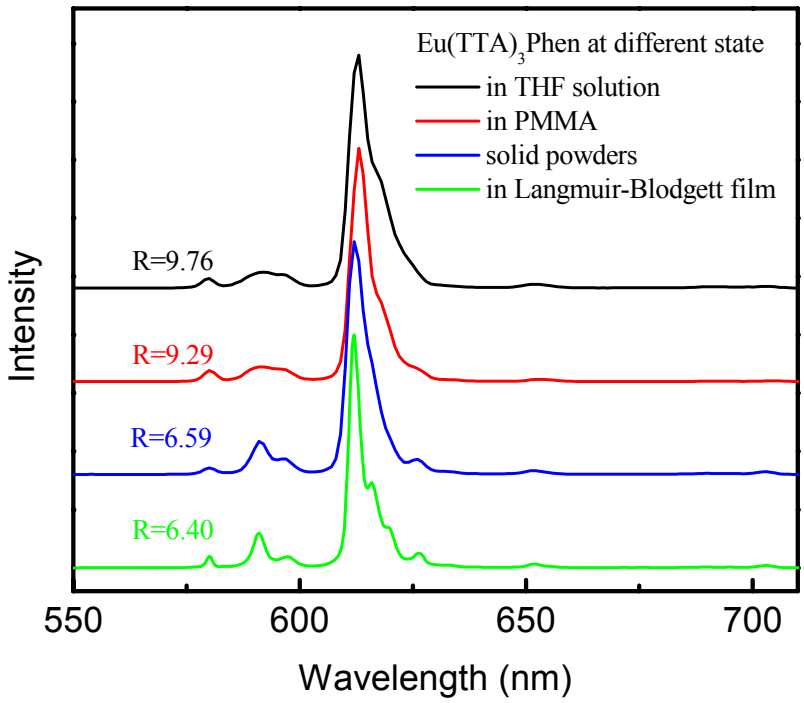

Figure S2 Fluorescence spectra of $Eu(TTA)_3Phen$ in THF solution, $Eu(TTA)_3Phen$ doped PMMA film ($Eu(TTA)_3Phen$ concentration is 3 wt %), $Eu(TTA)_3Phen$ powders and $Eu(TTA)_3Phen$ in Langmuir-Blodgett film. The data of $Eu(TTA)_3Phen$ doped PMMA and $Eu(TTA)_3Phen$ in Langmuir-Blodgett film are taken from our previous work.[1, 2]

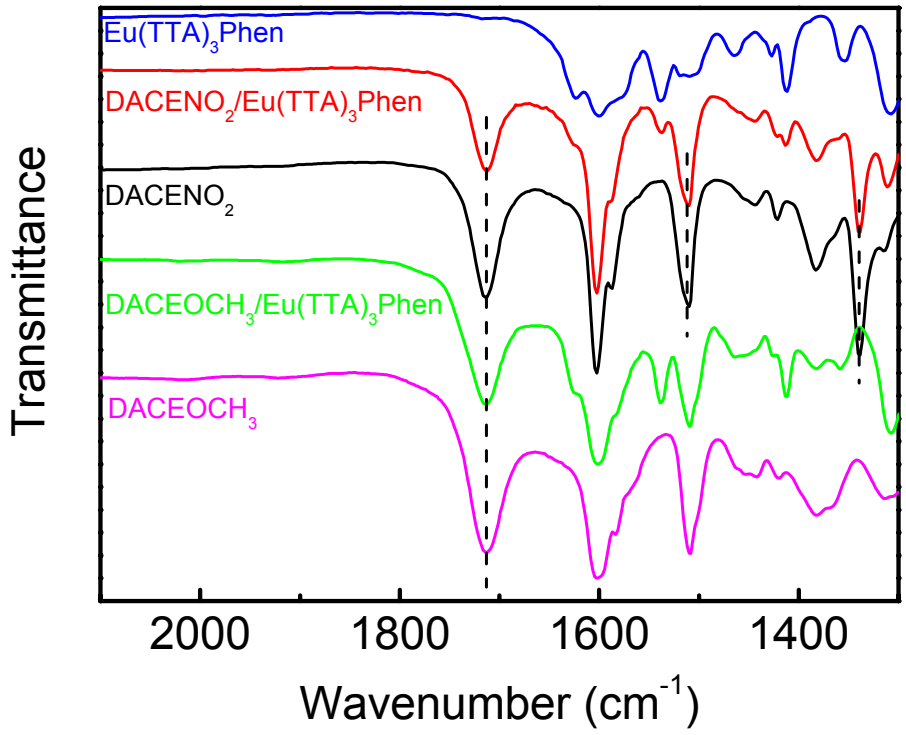

Figure S3 FT-IR spectra of $Eu(TTA)_3Phen$, $DACENO_2/Eu(TTA)_3Phen$, $DACENO_2$, $DACEOCH_3/Eu(TTA)_3Phen$ and $DACEOCH_3$. The peaks of carbonyl groups and nitryl groups did not change. This means there is no coordination interaction between the polymer matrices and Eu^{3+}.

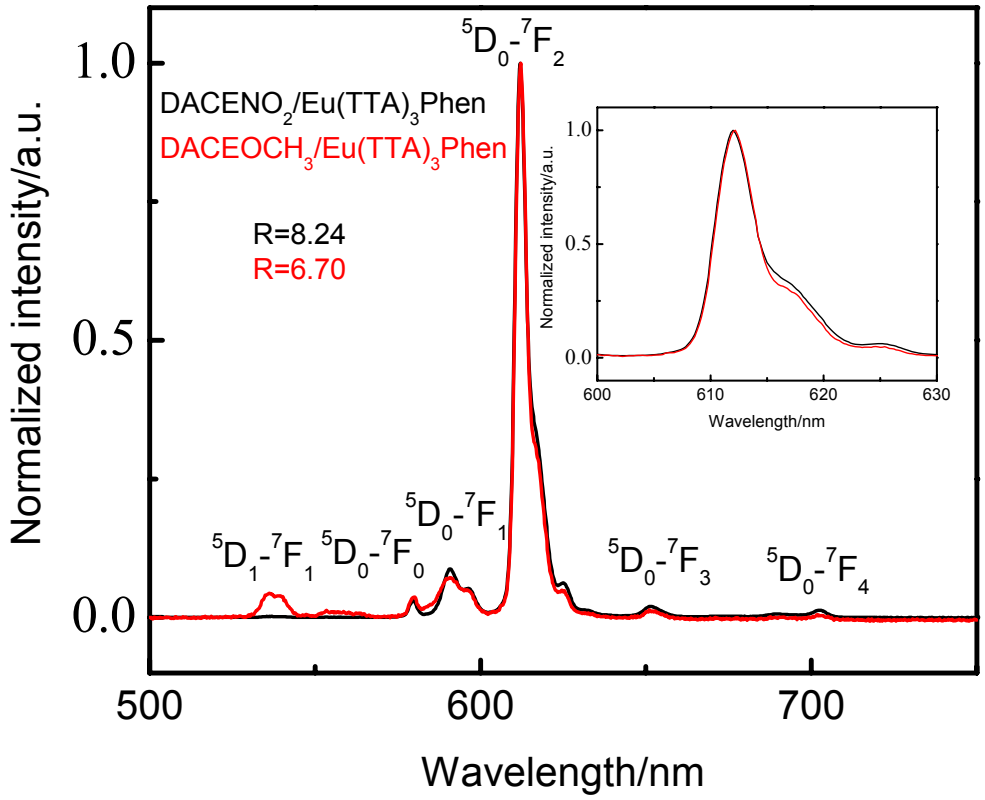

Figure S4 Intensity-normalized fluorescence spectra of DACENO$_2$/Eu(TTA)$_3$Phen film and DACEOCH$_3$/Eu(TTA)$_3$Phen film. The inset is the enlargement of $^5D_0 \rightarrow {}^7F_2$ transition. It can be clearly seen that there is some differences in $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transition of Eu(TTA)$_3$Phen in the two films. Besides the differences in $^5D_1$-$^7F_1$ transitions and $^5D_0$-$^7F_2$/$^5D_0$-$^7F_1$ relative intensity ratio, this is the third proof that the local environment of Eu^{3+} in the two films is different.

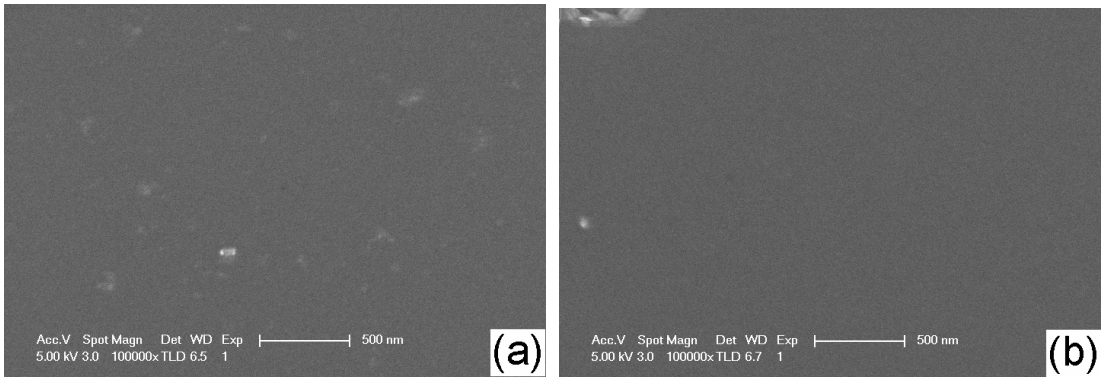

Figure S5 SEM images of (a) DACENO$_2$/Eu(TTA)$_3$Phen film and (b) DACEOCH$_3$/Eu(TTA)$_3$Phen film.

Table S1 shows the theory calculation on the radiation parameters of the two films. Judd-Ofelt theory is employed to calculate these parameters.[3, 4] The detailed calculation process is reported in our previous work. [1, 5]

Table S1

(a) Radiative parameters of $DACENO_2/Eu(TTA)_3Phen$ film

R=8.24 $\Omega_2=12.44\times10^{-20}$ cm^2 $\Omega_4=0.38\times10^{-20}$ cm^2

Emission transition	ν (cm^{-1})	A_{ed} (s^{-1})	A_{md} (s^{-1})	A (s^{-1})	β (%)	σ (10^{-22} cm^2)
$^5D_0\rightarrow{}^7F_0$	17247	0	0	0	0	0
$^5D_0\rightarrow{}^7F_1$	16932	0	75.93	75.93	10.68	4.55
$^5D_0\rightarrow{}^7F_2$	16340	625.62	0	625.62	88.04	59.48
$^5D_0\rightarrow{}^7F_3$	15352	0	0	0	0	0
$^5D_0\rightarrow{}^7F_4$	14237	9.09	0	9.09	1.28	1.43
A_T (s^{-1})				710.64		
Radiative lifetime τ_{rad} (ms)= 1.41 ms						

(b) Radiative parameters of $DACEOCH_3/Eu(TTA)_3Phen$ film

R=6.70 $\Omega_2=10.10\times10^{-20}$ cm^2 $\Omega_4=0.35\times10^{-20}$ cm^2

Emission transition	ν (cm^{-1})	A_{ed} (s^{-1})	A_{md} (s^{-1})	A (s^{-1})	β (%)	σ (10^{-22} cm^2)
$^5D_0\rightarrow{}^7F_0$	17235	0	0	0	0	0
$^5D_0\rightarrow{}^7F_1$	16920	0	75.77	75.77	12.80	3.39
$^5D_0\rightarrow{}^7F_2$	16335	507.48	0	507.48	85.78	50.07
$^5D_0\rightarrow{}^7F_3$	15361	0	0	0	0	0
$^5D_0\rightarrow{}^7F_4$	14241	8.38	0	8.38	1.42	0.98
A_T (s^{-1})				591.63		
Radiative lifetime τ_{rad} (ms)=1.69 ms						

The Judd-Ofelt parameters Ω_2, Ω_4 are presented in Table S1. Ω_6 is not presented because the $^5D_0\rightarrow{}^7F_6$ transition could not be experimentally detected. This indicates Ω_6 is not important here. The large values of Ω_2 indicate the presence of covalent bonding between the Eu^{3+} and the surrounding ligands.[6] The strong hypersensitive transition $^5D_0\rightarrow{}^7F_2$ accounts for such Ω_2 values. The Ω_4 parameters have been related together to bulk properties of the lanthanide-based hosts, but there is no theoretical prediction for this sensibility to macroscopic properties.[7] The quality of the host material for lasing action of Eu^{3+} is often expressed through R or Ω_2 values.[8] According to the calculation equations[1, 5], there is a relationship between Ω_2 and stimulated emission cross section. The Ω_2 of $DACENO_2/Eu(TTA)_3Phen$ is bigger than that of $DACEOCH_3/Eu(TTA)_3Phen$. The stimulated emission cross section of $DACENO_2/Eu(TTA)_3Phen$ is also bigger than that of $DACEOCH_3/Eu(TTA)_3Phen$. The $^5D_0\rightarrow{}^7F_2$ transition shows the highest fluorescence branching ratio value in both films. It has already been established that an emission level with fluorescence branching ratio value near 50% becomes a potential laser emission transition.[9] And our results are

88.04% for $DACENO_2/Eu(TTA)_3Phen$ and 85.78% for $DACEOCH_3/Eu(TTA)_3Phen$, which are much higher than 50%. In addition, the stimulated emission cross section of $^5D_0 \rightarrow {}^7F_2$ of the two films are 59.48×10^{-22} cm^2 and 50.07×10^{-22} cm^2 which are higher than Europium complex doped PMMA, in which optical amplification effect is observed.[10] All these results showed that the films have highly fluorescent efficiency and the $^5D_0 \rightarrow {}^7F_2$ transition can be considered as a possible laser transition and can be used in optical amplification. $DACENO_2$ is better than $DACEOCH_3$ because the Judd-Ofelt parameters listed in Table S1 indicated $DACENO_2/Eu(TTA)_3Phen$ has better radiation properties and $Eu(TTA)_3Phen$ emits stronger red light in $DACENO_2$.

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