Luminescent Films with Spectral and Temporal Encoding for Advanced Anti-Counterfeiting Security

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Luminescent materials invisible to the naked eye but detectable under ultraviolet radiation have been applied as anticounterfeiting tags of documents and products. Eu^{II}-based phosphors exhibiting persistent luminescence and Eu^{III} complexes displaying conventional luminescence have stood out for such a proposal. However, the dissemination of knowledge about these technologies may enable counterfeiters to develop methods to imitate or bypass these security mechanisms. To work around this issue, this investigation seeks to fabricate polymeric films containing two different security codes: (1) emission color change as a function of the excitation wavelength and (2) emission color change as a function of time after turning off the excitation source. To accomplish such task, transparent films were synthesized by using polymethyl methacrylate (PMMA) as polymer matrix, $SrAl_2O_4:Eu^{II},Dy^{III}$ as the persistent luminescence material, and the complex $[Eu(nta)_3(phen)]$ (nta = 4,4,4-trifluoro-1-(2-naphthyl)-1,3-butadione; phen = phenanthroline) as the conventional luminescent emitter. Upon 380 nm excitation, only the typical Eu^{III} luminescence is noticed within the red spectral window while at 450 nm excitation, the Eu^{II} luminescence in the green is observed. Upon 400 nm excitation, both Eu^{II} and Eu^{III} luminescence is detected, leading to a yellow-orange emission color. This result shows that the emission color output can be tunned from red to green, crossing the yellow, by changing the excitation energy. Interestingly, after ceasing the excitation energy at 380 nm, the emission color shifts from red (Eu^{III} luminescence) to green owing to the persistent luminescence of $SrAl_2O_4:Eu^{II},Dy^{III}$. Therefore, these results demonstrate that combining $SrAl_2O_4:Eu^{II},Dy^{III}$ and $[Eu(nta)_3(phen)]$ is a promising strategy for developing security codes with emission color outputs featuring both spectral and temporal encoding, thereby making the falsification process significantly more challenging.

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