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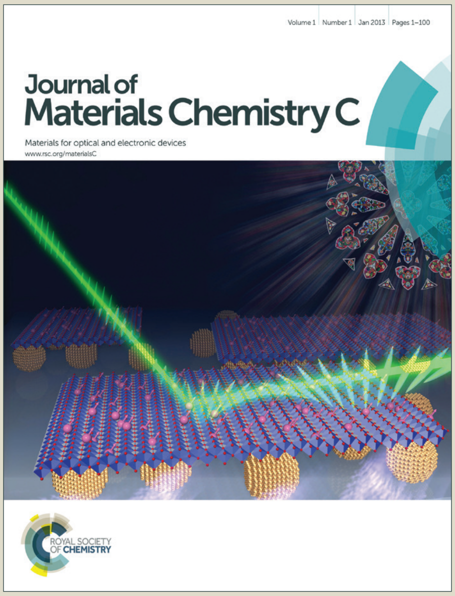

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Novel up-conversion luminescent rare-earth doped organic resins for cost-effective applications in 3D photonic devices

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Up-conversion luminescent materials have been recently emerging for the improvement of photocatalytic activity of semiconductor electrodes, such as TiO_2 and Fe_2O_3, used for sustainable production of hydrogen via water-splitting. Here we present novel up-conversion luminescent organic resins doped with heavy rare-earth ions, which are used as constructive elements in the 3D technique, that open a fully unexplored highway for the development of cost-effective, room-temperature and endless shape 3D photonic structures, avoiding technical difficulties of glass melting or crystals growth when used as rare-earth hosts. Moreover these synthesized resins also present outstanding UV-VIS up-conversion luminescence of Er^{3+} and Tm^{3+} ions sensitized by Yb^{3+} ions under near-infrared excitation at 980 nm, and have been extensively analyzed as a function of doping concentration. Furthermore the increase in the Yb^{3+} to Er^{3+} and Tm^{3+} ratio results in a noticeably enhancement of UV-blue high energetic emission bands, tailoring the overall up-conversion luminescence to match different band-gaps of selected photocatalysts.

Introduction

Materials presenting efficient up-conversion luminescence, which convert photons from the near infrared into the UV-visible, show up as important candidates for different technological applications, such as short wavelength solid state lasers, biological fluorescence labels, high density optical data storage, enhanced response solar cells and white light generation [1-3]. Moreover these up-conversion luminescent materials, which transform the unused red and near-infrared into available UV-VIS, extend the spectral response of semiconductor electrodes (TiO_2 and Fe_2O_3) as a solely photonic approach to enhance photocatalytic activity [4-8] for sustainable production of hydrogen using a photo-electrochemical (PEC) water-splitting cell [9,10]. The resulting hydrogen can be stored or it can provide power from highly efficient fuel cells [11] producing water as final by-product comprising a solar and water-driven sustainable closed circle to face the terawatt carbon-neutral challenge and the global warming threatening.

Rare-earth ions (RE) are key elements for efficient up-conversion generation due to their long lifetime excited states, narrow spectral lines and particular energy level diagram with multiple emissions in the visible range. Among them, Yb^{3+} ions act as a very efficient infrared antenna, harvesting IR photons due to their unique long lifetime excited level with a very large absorption cross-section at around 1 μm ($^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition), resonant with commercial available cheap laser diodes and therefore a very convenient wavelength to test the capability to transform the IR radiation into UV-VIS for further applications in enhancing photocatalytic activity [6,12,13]. Moreover, Yb^{3+} also shows up as one of the best known suitable sensitizer for other RE ions, such as Er^{3+} and Tm^{3+}, due to subsequent efficient energy transfer, giving rise to UV and VIS up-conversion emissions. Therefore, the combination of Yb^{3+}-Er^{3+}-Tm^{3+} origin the efficient simultaneous red, green and blue UC emissions, yielding to generation of white light, and also to important high energetic UV emissions [14].

There has been a strong interest in organic-inorganic hybrid materials where RE-doped compounds are embedded in organic polymer host matrices [15,16] as well as other up-conversion pairs also embedded in multicomponent polymeric organic solid films [17-22]. In this sense these organic hosts show up as ideal for a cost-effective and fast approach, replacing other conventional high-temperature methods of incorporation of RE ions into melted glass matrices or crystals, for their incorporation into a photo-sensible organic material at room temperature. Moreover, the 3D micro fabrication method via the microstereolithography (μSL) technique uses these types of photo curable organic resins [23-26]. In this procedure, a microstructure is built, layer by layer, by tracing a focused light beam on defined areas in a photo-sensitive organic resin bath to produce polymeric layers.

Therefore, in this work we report for the first time to our knowledge the inclusion of heavy rare-earth ions into this type of photo curable organic resin hosts, presenting efficient VIS up-conversion luminescence and even comprising high energetic UV-blue emissions. These novel up-conversion organic resins open a fully unexplored highway for the design and development of luminescent materials with any specific designed patterning using a cost-effective 3D-printing system; that is, ease shapely and manufactured with a room-temperature method, lowering elaboration times and costs. This approach suggests a wide range of promising applications in plastics, paintings, coatings and new structures for up-conversion powered heterogeneous photocatalysis reactors and PEC devices.

Experimental

We selected the poly(ethylene glycol) diacrylate (PEGDA) as photo curable organic resin for the samples prepared in this work, and the Irgacure819 as the UV sensible photoinitiator.

Two sets of RE-doped organic resin pellets were prepared: the first one, taking a constant amount of resin (about 0.5g) and adding a variable total quantity of a rare-earth (RE) combination (with a fixed Yb^{3+}:Er^{3+}:Tm^{3+} ratio, 7:1:1). This resulted in three pellets with different relative mass ratios between the organic resin and the RE mixture; i.e, 3, 6 and 12, and henceforth will be labeled as H (High), M (Medium) and L (Low) pellets, respectively.

Finally, in a second set, keeping again the same amount of organic resin (about 0.5g), but varying the relative ratio between the Yb^{3+}:Er^{3+}:Tm^{3+} dopants in the RE mixture, from 1:1:1 to 10:1:1, in order to compare the variation in the up-conversion emissions and their close relationship with the amount of Yb^{3+} as a sensitizing infrared antenna.

In all the cases, the dispersion of RE ions into de photo sensible materials turns into solid after been exposed to a white source of light from an Optoma DLP projector, for just 2 seconds.

Optical absorption spectra of RE-doped organic resins were measured by an ultraviolet-visible-infrared (UV-VIS-IR) spectrophotometer Perkin-Elmer Lambda 9 with a resolution of 0.5 nm. Up-conversion measurements were carried out with a continuous wave laser diode at 980 nm with a power up to 300 mW, focusing by a 4X micro-objective, with a focal length of 4.51 mm and 0.55 of numerical aperture, which allows obtaining the power density of about 20 W/cm^2 at the sample surface measuring the FWHM incident beam width, as achieved by the authors in previous works [27]. Detection was obtained through a 0.25 m monochromator equipped with a photomultiplier. CCD digital camera was used to take colour pictures of up-conversion luminescence emitted by the samples. A compromise between exposure time and brightness control has been taken into account in order to avoid saturation of the CCD. All spectra were collected at room temperature and corrected by the instrumental response.

Results and discussion

Figure 1 presents the VIS and NIR absorption spectra of (a) an undoped and (b) a RE-doped (Yb^{3+}-Er^{3+}-Tm^{3+}) organic resin (H pellet), where assignation to transitions from the ground to excited states for the Er^{3+}, Tm^{3+} and Yb^{3+} ions are labelled, according with their respective energy levels in Fig. 2.

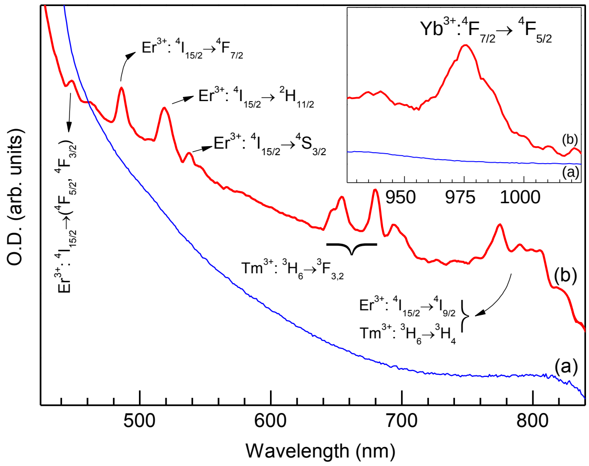

Fig. 1. Absorption spectra of (a) an undoped and (b) a RE-doped (Yb^{3+}-Er^{3+}-Tm^{3+}) organic resin, in some parts of the visible and NIR range, where the large cross-section of Yb^{3+} ions (inset) act as infrared collecting antenna.

It can be clearly seen how the incorporation of RE dopants into the organic resin is clearly evidenced by the appearance of characteristic absorption peaks, superposed to the smooth baseline of the resin host, which are related to the corresponding RE electronic transitions. In particular, on one hand, main transitions of Er^{3+} and Tm^{3+} are observed in the VIS range (400-850nm), and on the other hand, in the NIR range at around 980 nm, the unique and strong transition of the Yb^{3+} element is depicted. This large absorption cross-section $^2F_{7/2}\rightarrow^2F_{5/2}$ transition (see energy level diagram of Fig. 2) would act as a sensitizing infrared antenna for activating UV-Visible up-conversion emission, as will be presented below. Main up-conversion emissions and corresponding mechanisms by energy transfer processes between RE dopants are clearly depicted in the energy level diagram of Yb^{3+}, Tm^{3+} and Er^{3+} ions in Fig. 2. As it can be seen, Yb^{3+} sensitizing infrared antenna mainly absorbs the 980 nm pump, giving rise to UV-VIS up-conversion emissions after suitable efficient energy transfer to the emitting Tm^{3+} and Er^{3+} ions.

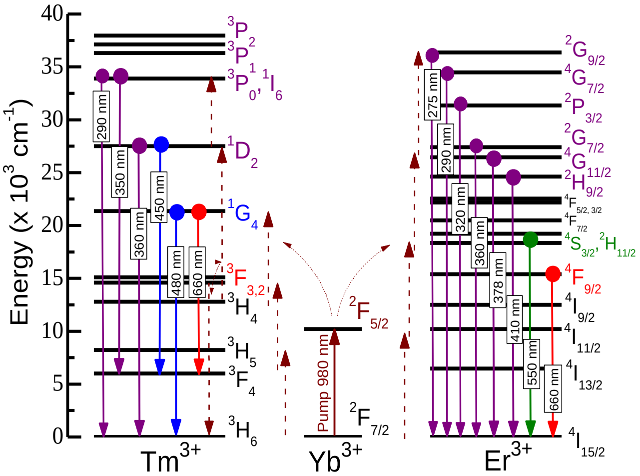

Fig. 2. Energy level diagram of Yb^{3+}, Tm^{3+} and Er^{3+} ions. Up-conversion mechanisms, pumping and main emission transitions are arrowed and labelled with corresponding wavelengths.

Figure 3 presents the up-conversion luminescence spectra of the H, M and L pellets under 980 nm laser excitation at 300 mW within the blue-greenish range, i.e, from 440-570 nm. Those spectra have been normalized to the 660 nm (not shown) in order to highlight the enhancement of the main blue and green emissions (centred at 475 and 545 nm) when decreasing the RE concentration partitioned in the organic resin, from the H to the L pellet. In the same way, the UV-blue up-conversion luminescence spectra of the H, M and L pellets are depicted in Fig. 4. It can be also seen again how the most energetic up-conversion emissions are noticeably enhanced when the RE concentration of the pellet decreases resulting, in particular for the L pellet, in outstanding UV blue up-conversion emissions coming from the $^1I_6$ and $^1D_2$ level of Tm^{3+} ions, not very often reported in literature. This fact would imply interesting applications since it proves that up-conversion emissions are boosted with decreasing RE concentration, probably due to the avoid of cross-relaxation among RE ions reducing concentration quenching effects. Therefore it would involve the use of lower quantities of RE dopants as a cost-effective approach for synthesising these novel up-conversion luminescence resins.

It should be emphasized here that these high energetic UV-blue up-conversion emissions in RE-doped systems have been lately proved by the authors to accelerate the decomposition of pollutants by a 20% improvement of the photocatalytic action of the commercial benchmark TiO$_2$ efficient photocatalyst in the decomposition of methylene blue in water, and also by 2.5 times enlargement of the photolytic degradation rate [8].

Therefore, the intense UV-blue and also the green up-conversion luminescence of the RE-doped organic resins here reported opens a very promising roadway for the developing of highly efficient solar active photocatalyst, extending the spectral response of main water-splitting semiconductor electrodes such as TiO$_2$ [7,8] and also as hematite (Fe$_2$O$_3$), with a recently growing as a promising rare-earth abundant photocatalytic semiconductor [6,28].

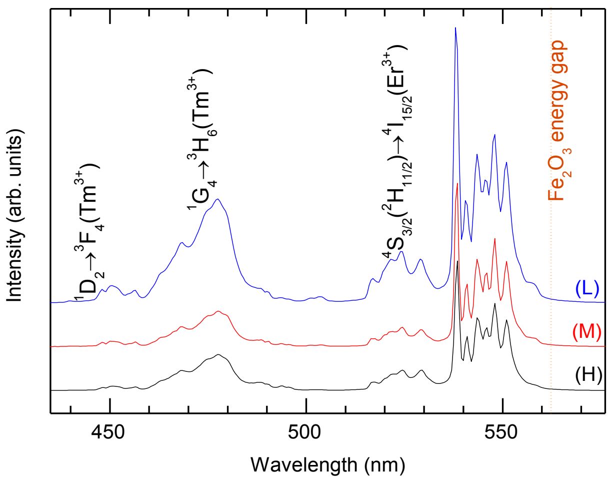

Fig. 3. Visible up-conversion luminescence spectra under 980 nm laser excitation (at 300 mW) of different organic resins with varying doping level of heavy rare-earth ions (Yb^{3+}-Er^{3+}-Tm^{3+}): (H) high, (M) medium and (L) low concentrated pellets. Position of bandgap for Fe$_2$O$_3$ photocatalytic semiconductor material is also depicted. Spectra are normalized to the Er^{3+} and Tm^{3+} emission at 660 nm (not shown).

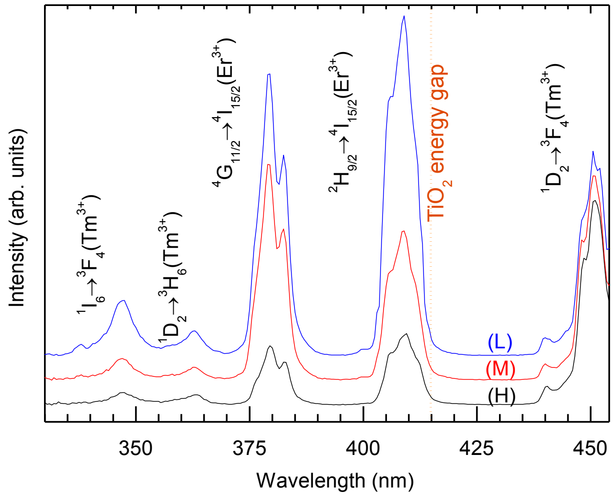

Fig. 4. UV-blue up-conversion luminescence spectra under 980 nm laser excitation (at 300 mW) of different organic resins with varying doping level of heavy rare-earth ions (Yb^{3+}-Er^{3+}-Tm^{3+}): (H) high, (M) medium and (L) low, respectively. Spectra have been normalized at the 450 nm emission. Position of bandgap for the main photocatalytic semiconductor material used in water-splitting, TiO$_2$, is also depicted.

Moreover, for quantifying up-conversion emission we have followed the method developed by J. F. Suyver et al. [29], where the intensity of the up-conversion emissions is characterized in terms of photon flux units of the spectra through a comparative area calculation. In that respect, we have calculated that in the L pellet approximately the 9% of the total up-conversion emission can bridge the gap of Fe$_2$O$_3$.

Next, we present corresponding photographs for a set of these novel RE-doped upconversion luminescent organic resins (Fig. 5) comprising the H and L pellets (5a and 5b, respectively) and also a low RE-concentrated resin deposited as a laminar thin layer between two glass plates (5c).

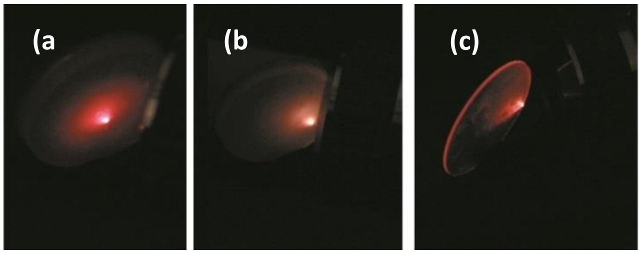

Fig. 5. Photograph of a set of novel RE-doped up-conversion luminescent resins: H high (a), and L low (b) concentrated pellet. Moreover a low concentrated resin deposited as a laminar thin layer between two glass plates is also shown (c). All three samples show strong up-conversion luminescence under focused 980 nm infrared laser excitation at 300 mW.

It can be seen at naked eye the appreciable slight change of the overall emitting colour when comparing the H (Fig. 5a) and the L pellet (Fig. 5b), turning from a reddish into a more whitish apparent colour. This is an expected consequence of the remarkably increment in the high energetic upconversion emissions in the blue region with decreasing RE-concentration from H to L pellet, according to the spectra shown in Fig 3 and 4. Moreover, the intense up-conversion emission is even displayed by a thin layer of these luminescent resins, shown in Fig. 5c, which points to their potential interest in a wide range of applications such as paintings and coatings of photonic devices.

Moreover, we have also analysed the effect of increasing the ratio of the sensitizer Yb^{3+} concentration with respect to the emitting Er^{3+} and Tm^{3+} ions. Therefore two different organic resins pellets have been synthesized varying the relative ratio between the Yb^{3+}:Er^{3+}:Tm^{3+} dopants in the RE mixture, from 1:1:1 to 10:1:1, in order to evaluate the effect of the Yb^{3+} as an infrared absorbing antenna. Figure 6 comprises corresponding photographs of these two different RE-doped organic resins along with their respective up-conversion luminescence spectra under infrared 980 nm laser excitation at 300 mW. As above mentioned, the role of the Yb^{3+} ions in the mechanism of the up-conversion processes (visibly depicted in the energy level diagram of Fig 2) is reflected in the increase of the high energy up-conversion emissions (375-475 nm) as clearly observed in the inset spectra of Fig. 6. Thus, the Yb^{3+} ions, whose aggregate acts as an infrared collector, harvest the long wavelength infrared photons [30]. This fact allows a tuneability of the emitting colour [31] from orange-reddish to purplish when Yb:Er:Tm ratio changes from 1:1:1 to 10:1:1 (Fig 6a and 6 b, respectively), and therefore enables the tailoring of the up-conversion emissions to match different energy band-gaps of any selected water-splitting semiconductor electrode, as also represented in Fig. 6 for Fe_2O_3 and TiO_2. In that sense we also have calculated the respective colour coordinates (x,y) of the total visible luminescence in terms of the CIE standard chromaticity diagram formalism [32]. The appreciable variation of these values from (0.5618, 0.3954) for the 1:1:1 pellet to (0.5307, 0.3223) for the 10:1:1 shows the potential of these resins as tuneable up-conversion phosphors, see Fig. S1 in Supporting Information.

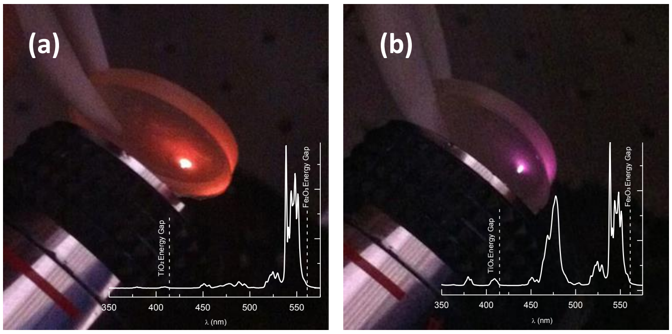

Fig. 6. Photograph of two different RE-doped organic resins with (a) 1:1:1 and (b) 10:1:1 Yb^{3+}:Er^{3+}:Tm^{3+} ratio, showing strong up-conversion luminescence under infrared 980 nm laser excitation at 300 mW, along with their respective spectra where the band gaps of main photocatalytic semiconductors (TiO_2 and Fe_2O_3) are also depicted.

Finally, and as an example of the potential possibilities of these novel up-conversion resins in the μSL 3D-printing technique, we have produced a 3D-printed model shaped as a PEC water-splitting cell, see photograph in left-hand side of Figure 7. This exemplification illustrates the use of the new RE-doped organic resins for coating or even fabricating any device showing strong up-conversion luminescence (right-hand side of Fig. 7) with potential effect in the enhancement of photocatalytic activity [4-6] as verified by the authors [8]. Hence, these novel intense UV-blue emitting organic resins lead the way for their implementation in PEC devices for an enhanced production of hydrogen due to the extended spectral response of the photocatalysts.

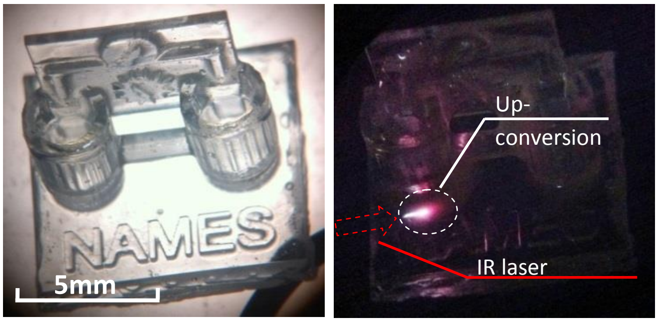

Fig. 7. Photograph of a 3D-printed model shaped as a photo-electrochemical (PEC) cell using these new RE-doped up-conversion organic resins. NAMES logo stands for our research group, nanomaterials and spectroscopy, www.names-ull.es.

Conclusions

We have reported here the synthesis of novel up-conversion luminescent organic resins, doped with heavy rare-earth ions (Yb^{3+}-Er^{3+}-Tm^{3+}) for the first time to our knowledge, which are used as constructive elements in the 3D micro fabrication method with the microstereolithography (μSL) technique. Furthermore these luminescent resins present outstanding UV-VIS up-conversion emissions that open important alternative routes for the development of cost-effective 3D photonic structures, avoiding technical complications related to glass melting or crystals growth when used as luminescent hosts for rare-earth ions. Additionally the spectroscopic analysis reveals the possibility of tuning the emission by changing the rare-earth concentration and the corresponding ratio between dopants, to tailor the overall up-conversion luminescence for matching different band-gaps of selected photocatalysts used in photo-electrochemical water-splitting devices.

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In Memoriam, Dr. Victor Tikhomirov (1961-2014) for your valuable discussions and expertise in luminescence of rare-earths during all these years, спасибо товарищ.

Notes and references

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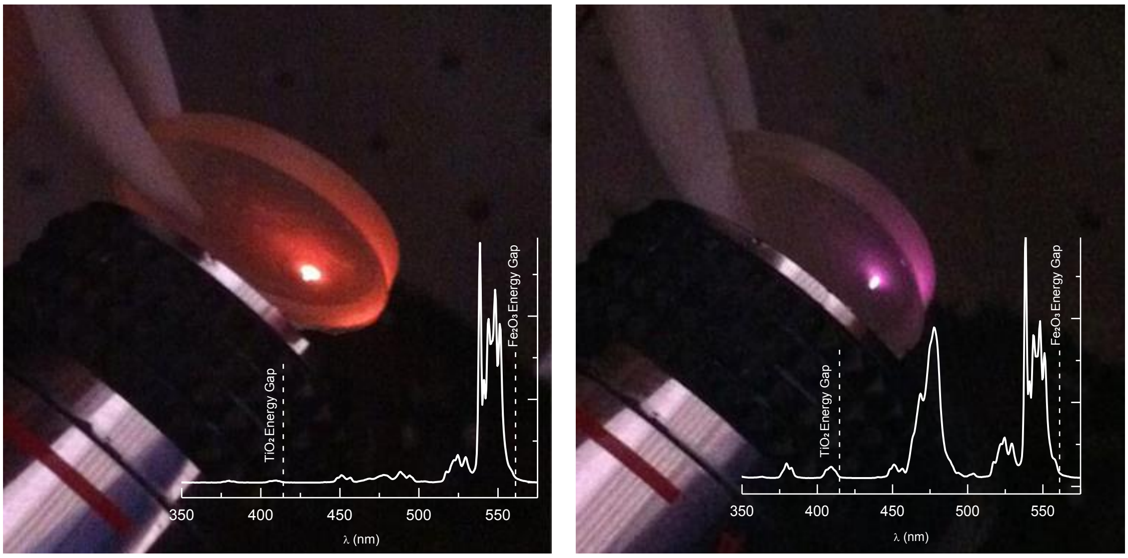

Novel up-conversion luminescent RE-doped organic resins with varying Yb^{3+}:Er^{3+}:Tm^{3+} concentration ratio, along with corresponding emission spectra under infrared 980 nm laser excitation, tailoring the overall up-conversion luminescence to match different band-gaps of main photocatalytic water-splitting semiconductors (such as TiO_2 and Fe_2O_3, also depicted). They open a fully unexplored highway for the development of cost-effective, room-temperature and endless shape 3D photonic structures, avoiding technical difficulties of glass melting or crystals growth for conventional rare-earth hosts.