Annihilation assisted upconversion: all-organic, flexible and transparent multicolour display

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Abstract. In this paper, we demonstrate the first all-organic, transparent, flexible, versatile colour displays based upon triplet–triplet annihilation assisted photon energy upconversion in viscous polymeric matrix. The devices work with ultra-low excitation intensities down to 20 mW cm$^{-2}$ red or near-IR light. The displays are based on metallated-porphyrin sensitizers in combination with emitters dispersed in a transparent polymeric matrix and are driven by galvo-scanned laser diodes. The displays have external quantum yield as high as 3.2%. The response time can be adjusted to specific application requirements—up to 80 $\mu$s allowing kHz-refreshment rate of the displayed information. It is possible to easily tune the optical density of the screens in order to obtain a desired transmittance for the excitation beam. We demonstrate the ability to achieve multicolour emission, using only one excitation source. There are practically no display size limitations.

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1. Introduction and background

The common principle used in static 2D- and 3D-upconversion (UC) displays is the sequential absorption of two or more photons followed by consecutive energy transfer in rare-earth-ion doped solids [1]–[3]. The process of UC in ion-doped systems suggested originally by Bloembergen [4] later has been observed in various types of ion-doped solids such as crystals and glasses in bulk, fibre or waveguide form [5]. The advantage of this approach is that there are very few hidden zones, which leads to a wide field of view. The first disadvantage of ion-doped UC systems is the relatively low integral UC emission and the limitations, arising from the needed moderate (tens of kW cm\(^{-2}\)) to high (MW cm\(^{-2}\)) excitation intensity. Therefore, the application range of these UC displays is inherently limited: even at moderate, but realistic scanning conditions [2] the required excitation intensity overcomes the damage threshold of most optical materials.

The second disadvantage of the ion-doped UC displays is the complicated technology of scaling of the devices: in the case of heavy metal fluoride glasses [2] doped with rare earth ions, the samples with optical quality have relatively small size (of the order of \(1 \times 10^{-2}\) m); in the case of rare earth ions doped glassy-UC-powders, distributed in a polymer matrix, the devices obtained have a huge diffuse scattering properties. The displays obtained are not transparent and in some examples almost 50% of the pumping optical power is back scattered [3]. So, the huge amount of laser light transmitted or scattered from the UC displays [2, 3] must be suppressed effectively (for security reasons), which additionally complicates the application of these types of UC devices.

2. Materials and methods

In the context of luminescent display applications, the triplet–triplet annihilation (TTA)-supported bimolecular photon UC process has a fundamental advantage [7, 8]: the necessary excitation intensity is drastically lowered—intensities in order of 20 mW cm\(^{-2}\) are sufficient to create a bright, easily observable image. Another principal advantage of this UC process is the excellent external quantum yield of more than 3% (in classical means (see footnote 4)) realized.

The integral UC-emission regarding the excitation for the ion-doped screens reported in [2, 3] could be estimated to approximately \(10^{-4} - 10^{-5}\), for comparison, the integral UC-emission of the TTA-based screen reported in our work is estimated as \(\sim 10^{-2}\).

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Figure 1. (a) Energetic schema of the TTA supported UC process; structures of the sensitizer—PdPh₄TBP (b), the emitters perylene (c), BPEA (d), rubrene (e) and the matrix—styrene oligomers (f) used in this work.

with ultra-low excitation intensity [6]. Additionally, the devices are all-organic, flexible and transparent. There are no display size limitations defined by the materials.

A schematic representation of the process of photon UC based on TTA in multi-molecular system is shown in figure 1(a). It has to be considered as an inherently connected chain of three already described processes [9]–[13]. The first process in the chain is the intersystem crossing (ISC), which is strongly enhanced by the spin–orbit coupling to the metal centre of metallated macrocycle sensitizer molecules [9, 10]. The efficient ISC within the sensitizer molecules (for instance the ISC-probability is almost 1 for the metallated porphyrins [11]) ensures a very efficient population of the sensitizer triplet level via single photon absorption.

On other hand, the very weak ISC of the emitter molecules (its probability for various anthracene derivatives has vanishing values [11]) substantially prohibits the depopulation of the excited emitter triplet states via phosphorescence and thus preserves the created triplet population of the emitter for the process of TTA. Therefore, very large difference between the ISC-coefficients of the sensitizer and emitter molecules must exist:

\[ c_{\text{ISC}}^{\text{sensitizer}} \gg c_{\text{ISC}}^{\text{emitter}} \]  \hspace{1cm} (1)

The second process in this chain is the transfer of the excitation of the sensitizer triplet to the emitter triplet (triplet–triplet transfer (TTT)) [12]. Formally, this process can be expressed...
through the equation:

\[ T_{\text{sensitizer}}^* + S_{\text{emitter}}^0 \rightarrow S_{\text{sensitizer}}^0 + T_{\text{emitter}}^*, \]  

(2)

where the superscripts * and 0 identify the first excited triplet state and the ground state, respectively. The efficiency of the TTT is predetermined by the extent of overlap of the sensitizer and emitter triplet manifolds:

\[ E_{\text{sensitizer}}^{\text{triplet}} \approx E_{\text{emitter}}^{\text{triplet}}. \]  

(3)

The third process is the subsequent TTA, which in our system occurs mostly between the triplets of the emitter molecules [13].

\[ T_{\text{emitter}}^* + T_{\text{emitter}}^* \rightarrow S_{\text{emitter}}^0 + S_{\text{emitter}}^* \rightarrow 2S_{\text{emitter}}^0 + h\nu. \]  

(4)

Here the superscripts * and 0 identify the first excited triplet or singlet state and the ground state, respectively. As a precondition for efficient energetically conjoined TTA–UC, there are two requirements related to the molecular structure of the emitter and the sensitizer molecules:

\[ 2E_{\text{emitter}}^{\text{triplet}} \geq E_{\text{emitter}}^{\text{singlet}}. \]  

(5)

This condition ensures that the added energy of two excited emitter triplet states is enough (without using thermal energy) to populate the first excited singlet state of the emitter molecule.

The last requirement for the UC system relates to the structure of the sensitizer absorption spectrum. In order to reduce the re-absorption of the generated UC emission from sensitizer molecules which are in the ground state, there should be a large enough ‘transparency window’. Metallated macrocycles like porphyrins and phthalocyanines have band-like absorption spectra grouped around two strong bands—the Soret-band and the Q-bands. Therefore, photons with energies lying far away enough from those two absorption maxima will be less absorbed. For instance, photons with energies around \( E \sim 2.3 \text{ eV} \) are not absorbed, when PdPh\(_4\)TBP is used as sensitizer. For the energy position of the absorption maxima of the sensitizer and the first excited singlet state of the emitter follows from the above:

\[ E_{\text{sensitizer}}^{\text{Soret-band}} > E_{\text{emitter}}^{\text{singlet}} \gg E_{\text{sensitizer}}^{\text{Q-band}}. \]  

(6)

To summarize all the above listed requirements for the multicomponent organic system: if the equations (1), (3), (5) and (6) are fulfilled, than the processes described in equations (2) and (4) will lead to very efficient energetically conjoined TTA–UC.

The structures of the sensitizer, meso-tetraphenyl-tetrazenoporphyrin palladium (PdPh\(_4\)TBP) and the emitters, dibenz[de,kl]anthracene (perylene), 9,10-bis(phenylethynyl)anthracene (BPEA) and 5,6,11,12-tetraphenylacene (rubrene), used in this work are shown in figures 1(b)–(e).

UC devices based on organic solutions [6]–[8] although showing relatively high external quantum yield (even non-coherently excited) are not suitable for display applications: sealing of these devices is not really efficient. As a consequence of the presence of the solvent, fast aging of the sealing layer is observed, followed by oxygen penetration and strong reduction of the UC efficiency. Exchanging the organic solvent (toluene) with a trimer/tetramer mixture of styrene oligomers (figure 1(f)) satisfies all requirements for efficient sealing. The quantum yields of the UC-couples studied in this work in oligomer solution and in organic solution (toluene) are comparable. The UC display also has a high durability—for a time period of 100 days, the device practically did not change its efficiency.
The absorption spectra of the sensitizer and emitters investigated in this work are shown in figure 2. The sensitizer has significant absorption in its Q-band (around $\lambda = 635$ nm). Also in figure 2 the absorptions of the corresponding emitters are shown as follows: perylene (navy line), BPEA (green line) and rubrene (orange line). It has to be pointed out that neither perylene nor BPEA nor rubrene singlet emission can be observed when these emitters are exposed to the red excitation light in their single solutions.

3. Results and discussion

The all organic colour 2D displays are shown in operation in figure 3. The images are created through a commercially available 2D galvo scanner and registered with a CCD device in daylight conditions. As excitation source a focused (with $d = 300$ $\mu$m beam waist) 10 mW diode laser ($\lambda = 635$ nm, single mode) is used. We have used frontal excitation, and as envisaged in figure 3, the scattering of the excitation beam is negligible. The colour displays are transparent (note that the tape holes of the optical table in figure 3 are clearly visible through the UC displays). The blue, green and orange displays are realized by using the UC couples as follows: PdPh$_4$TBP/perylene as blue emitter ($\lambda = 475$ nm and FWHM $\sim 25$ nm), PdPh$_4$TBP/BPEA as green emitter ($\lambda = 513$ nm and FWHM $\sim 50$ nm) and PdPh$_4$TBP/rubrene as orange emitter ($\lambda = 560$ nm and FWHM $\sim 75$ nm). The displays are made by using the doctor-blade technique, on extruded PS sheets (Goodfellow GmbH, 1.2 mm thickness), using separators with 250 $\mu$m thickness. All devices are prepared and sealed in a nitrogen filled glove-box. The concentrations of the emitter and sensitizer in all samples are constant, as follows $5 \times 10^{-4}$ M sensitizer (PdPh$_4$TBP) and $5 \times 10^{-3}$ M emitter (perylene, BPEA or rubrene). The UC spectra are shown in figure 4(a).
Figure 3. CCD-camera images (snapshots) of the running UC all-organic 2D-displays. Dimensions, 60 × 60 mm; polycarbonate sheets; frontal excitation, UC systems, as follows: (a) PdPh₄TBP/perylene, (b) PdPh₄TBP/BPEA and (c) PdPh₄TBP/rubrene. The mean excitation intensity is 25 mW cm⁻², λ = 635 nm, galvo-scanner sampling frequency (8 kHz) No blocking filters were used, daylight conditions.

Figure 4. (a) Normalized UC fluorescence spectra for sensitizer/emitter couples as follows: PdPh₄TBP/perylene (blue line), PdPh₄TBP/BPEA (green line) and PdPh₄TBP/rubrene (orange line). All UC-layer thicknesses are the same 250 µm. (b) Colour coordinates of the UC-displays reported in (a), regarding the CIE 1931 colour space chromaticity diagram (2-degree standard observer), as follows: for the PdPh₄TBP/perylene, x = 0.156, y = 0.305 (diamond); for the PdPh₄TBP/BPEA, x = 0.204, y = 0.559 (circle); for the PdPh₄TBP/rubrene, x = 0.500, y = 0.493 (triangle).

It is important to note that the display prototypes described above all work with one and the same excitation wavelength (λ = 635 nm). We have chosen these examples because they directly demonstrate the possibility of achieving three-colour UC displays using only one excitation laser. This fact inherently identifies the potential for pixelization of the display without using complicated multi-wavelength laser excitation schemes, as mentioned in [2, 3].
Figure 5. Rise-time and decay-time of the UC fluorescence displays, as presented in figure 2 after a 50 µs duration excitation pulse.

Figure 6. Rise-time and decay-time of the UC fluorescence, after a 100 µs excitation pulse. Excitation intensity 10 W cm$^{-2}$, $\lambda = 635$ nm (single mode diode laser), room temperature. UC-couple, PdPh$_4$TBP/BPEA in oligo-PS, with concentrations of $1 \times 10^{-4}$ M/ $1 \times 10^{-3}$ M (a) and $1 \times 10^{-3}$ M/ $2.5 \times 10^{-2}$ M (b).

The repetition rate with which one pixel of the TTA-based display could be optically accessed depends on both the rise-time and the decay-time of the UC fluorescence. In figure 5, the dynamic properties of the UC sensitizer/emitter couples used for the colour displays (as presented in figure 3) are shown. The rise-time of the UC fluorescence in viscous solution (oligo-PS) with the given concentration and at the used excitation intensity (10 W cm$^{-2}$) varies from about 35 µs to about 60 µs depending on the sensitizer/emitter couple. Accordingly, the
Figure 7. A flexible, UC all-organic 2D-display in operation. Dimensions, 100 $\times$ 60 mm; extruded PS-sheets (Goodfellow GmbH, 1.2 mm thickness), frontal excitation, UC-layer—250 $\mu$m thickness, UC system PdPh$_4$TBP/BPEA/oligo-PS. The excitation intensity is less than 20 mW cm$^{-2}$, $\lambda = 635$ nm, galvo-scanner sampling frequency 12 kHz. No blocking filters were used, daylight conditions. On the lab-wall, the poster based on publication [6] is clearly seen. (See the movie file available from stacks.iop.org/NJP/10/103002/mmedia.)

decay time of the annihilation UC fluorescence ranges from about 30 $\mu$s up to about 200 $\mu$s, also depending on the sensitizer/emitter couple (see figure 5). The difference in the rise-times represents the different time necessary for a transfer of the triplet population from the sensitizer- to emitter-triplet states and the filling of the emitter triplet reservoir. Other process characteristic parameters, such as triplet–triplet overlap between the sensitizer- and emitter-triplet states and the decay rate of the non-emissive decay channels for the excited sensitizer molecules also influences the rise-times. The decay time of the UC emission depends mostly on the strength of the TTA between the emitter triplets. All described parameters are specific for each sensitizer/emitter couple and the experimental conditions, such as absolute and relative concentration of the sensitizer and emitter molecules, excitation intensity, viscosity of the polymer matrix and local temperature. Therefore, by choosing the experimental conditions and the UC molecular couples, the response time of the UC displays can be controlled in broad intervals.

As an example of the wide tuning possibility for the pulse-to-pulse repetition rate the dynamic properties of two samples with different sensitizer/emitter concentrations of the same UC couple, namely PdPh$_4$TBP/BPEA are shown in figure 6. All other experimental conditions
for both samples are the same (including excitation intensity, viscosity of the matrix and temperature). The measurements are done using a streak camera (Hamamatsu C5680, single shot, slow mode).

As seen from figures 6(a) and (b) both rise-time and decay-time are strongly influenced by the concentration. For the more concentrated sample not only does the rise-time become shorter (decreasing from 130 $\mu$s down to 80 $\mu$s), but also the decay-time is significantly shortened from 400 $\mu$s down to 80 $\mu$s. In total, pulse-to-pulse repetition rate could be increased from 1.6 kHz up to 6 kHz. This possibility to control and optimize the pulse-to-pulse repetition rate with respect to the specific application is a further advantage of our all organic UC displays. For comparison, the rise- and decay-times for the rare earth ion-based displays are 100 $\mu$s to 600 $\mu$s, and $\sim$2000 $\mu$s, respectively [3], which allows only pulse-to-pulse repetition rates lower than 0.3 kHz.

Furthermore, by controlling the degree of re-absorption of the UC emission, it is possible to fine tune the emission spectrum of the displays. As seen in figure 6(a), at relatively low emitter concentration, the local emission maximum of the UC spectrum is at $\lambda = 485$ nm. Differently, at higher emitter concentration, the strongest UC emission maximum is at $\lambda = 513$ nm (figure 6(b)). This opens the possibility to vary, for instance, the ‘green’ colour of the display without changing the UC-couple. If a stronger change in the ‘green’ spectrum is needed then another UC couple can be used [14].

4. Conclusion

The all-organic UC displays reported here have no limitation for size scaling. The contrary, namely a very limited size scaling, is a common drawback for the UC screens based on rare earth-doped crystalline glasses reported so far [2, 3]. As we used all-optical scanning, any problems arising from the necessity to have fast moving parts of the screen [15] or high-acoustic levels, caused by gaseous/liquid laser breakdown [16], are not relevant.

To the best of our knowledge we demonstrate for the first time versatile colour all-organic and transparent UC displays. The reported displays are also flexible and have excellent brightness, as shown in figure 7. They show stable operation for more than 100 h. The optical density of the screens can be easily tuned, in order to obtain the required transmittance for the excitation beam regarding different applications. The response time of the device can be adjusted to specific application requirements in a broad temporal range—from a couple of $\mu$s up to hundreds of $\mu$s, allowing for kHz-refreshing rate of the displayed information. The display size would be limited mainly by the size of the optical substrates, although tiling would be fairly straightforward. The robustness of the materials allows efficient manufacturing techniques such as printing and roll-to-roll processing to be used.

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