Thermally switchable molecular upconversion emission

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ABSTRACT: In this work a novel strategy is introduced to achieve thermally switchable emission from photon upconversion systems based on organic dyes. By simply dissolving these molecules at low concentrations in phase-change media, a reversible, sharp and nearly complete interconversion from blue upconverted emission to red luminescence was observed around the solid-to-liquid transition of the system. This result was rationalized in terms of dye aggregation, which selectively occurs in the solid state and dramatically enhances the interchromophoric energy transfer processes leading to upconversion. Notably, this behavior is extendable to different media and dyes, which allows an easy tuning of the switching temperature and emission colors. In addition, by properly selecting the phase-change medium, our strategy permits facile preparation of solid molecular materials showing photon upconversion at room temperature and even at submicromolar dye concentrations.

INTRODUCTION

Photon upconversion (UC), the generation of high energy luminescence by sequential absorption of two or more photons of lower frequencies, has gained much attention in the last years for its potential applicability in several fields.[1-6] Although upconverting rare-earth particles are the most popular materials to realize this phenomenon,[7-9] their low and narrow absorption in the NIR and visible regions hampers their use in those applications requiring excitation with ambient light and low powers.[10-12] On the contrary, upconversion emission arising from sensitizer-emitter organic dye pairs interacting via triplet-triplet energy transfer (TTET) and triplet-triplet annihilation (TTA) processes, benefits from the large available range of highly absorbing and emitting chromophores spanning over the whole visible-NIR spectrum.[13-18] Furthermore, since relatively higher UC quantum yields (> 20%) can be reached by using non-coherent sources and light excitation intensities as low as 20 mW cm^{-2} (e.g. sunlight),[19-21] triplet-triplet annihilation upconversion (TTA-UC) represents a very appealing approach to be exploited in bioimaging[6,22-24] and photovoltaics.[25-27]

Currently, several advanced applications are being pursued for UC materials, such as white-light emission[28] and switchable luminescence.[29-37] In particular, achieving reversible control of photon upconversion upon application of external stimuli could be of impact in a variety of fields, such as spatial and temporal high-resolution fluorescence microscopy,[38-39] multicolor barcoding[29] and remote control of molecular photoswitching reactions.[30-31] The first reported switchable UC systems were based on rare-earth nanoparticles whose emission was partially or completely switched by tuning the power density of the incident NIR source,[30,32] by selectively irradiating bicomponent core-shell structures with dual excitation and emission properties[33] or by quenching nanoparticles luminescence via photochromic dyes anchored to their surface.[34] The requirements of high irradiation intensities, complex excitation schemes or intricate synthetic procedures to prepare hybrid photoresponsive systems represent important limitations of these rare-earth materials that are not overcome yet.[10-12,29-34]

In view of this, switchable TTA-UC has emerged as a promising alternative. Photoswitchable TTA-UC systems have only been very recently reported and rely on incorporating an additional photochromic unit to the triplet sensitizer and emitter system,[35-36] which may require complex design and/or preparation of the upconverting system, since the selected photochromic group must meet very tight optical and electronic conditions.[35-36] Alternatively, temperature-switchable TTA-UC emission systems have been reported lately. An elegant example was just described by Kimizuka and coworkers,[37] which is based on a reversible thermal gel-to-sol transition and the different solubility of molecular oxygen, a typical UC quencher, in the two phases. Even though UC emission was nearly inhibited in the sol phase due to higher oxygen solubility, the switch occurred gradually and required long heating times for the complete "on-off" behavior to take place. Moreover, this strategy might be hard to generalize if distinct switching temperatures are desired.

A simpler way to achieve thermal control of photon upconversion can rely on directly acting on the interactions between the excited sensitizer species and emitter molecules, since TTA-UC proceeds through two bimolecular energy transfer processes occurring at very short separation distances (< 1 nm).[13,14] Accordingly, for the most simple cases where sensitizer and emitter units are not chemically bonded, reducing or even blocking molecular diffusion upon cooling should enable inhibiting such energy transfer processes and, therefore, UC, as demonstrated in liposomes[40], polymer matrices[41] and liquid donor-acceptor mixture.[42] Aiming to develop a straightforward and universal method to achieve reversible temperature-responsive TTA-UC systems, we explored the general applicability of this strategy to simple phase-change materials (PCMs) such as organic solvents. While bimolecular TTET and TTA and, as such, UC emission could take place in the liquid phase of the PCMs, these processes should be prevented in the frozen state, thus resulting in an abrupt thermal transition between high-energy emitter fluorescence and low-energy sensitizer luminescence.

EXPERIMENTAL SECTION

Materials. 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine platinum(II) (PtOEP), 9,10-diphenylanthracene (DPA), 9,10-dimethylanthracene (DMA), 1,3,6,8-tetraphenylpyrene (TPPy), eicosane (EC) and poly(methyl methacrylate) (PMMA, MW = 350 kDa) were purchased from Sigma Aldrich and used as received. Toluene and dichloromethane (DCM) were obtained from Scharlab. Hexadecane (HD) was purchased from Alfa Aesar.

Preparation of solutions. DCM stock solutions of PtOEP, DPA, DMA and TPPy, with concentrations of 0.1 mM and 1 mM respectively, were prepared and stored in the dark to prevent photodegradation. Aliquots of these solutions were added to the appropriate amount of phase-change material to obtain the desired concentrations in the final mixtures. The volatile organic solvent added in this preparation process was finally removed under reduced pressure.

PMMA film preparation. 0.25 g of PMMA were dissolved in 5 mL of a DCM dye solution ([PtOEP] = 0.04 μM, [DPA] = 1.26 μM). The prepared solution was casted onto a glass Petri plate and DCM evaporated overnight yielding a PMMA film with dyes concentration of 1 μM (PtOEP) and 30 μM (DPA).

Optical characterization. UV-Vis absorption spectra of the dyes were registered in a Varian Cary 4000 spectrometer. Temperature-dependent emission experiments and time resolved measurements were carried out by irradiating the sample at 532 nm with a pulsed Quantum Brilliant B Nd:YAG nanosecond laser. Because of the solvent phase change during the temperature variation and the formation of solid non-transparent materials, the emission measurements were carried out in reflectance mode using a 1 cm x 2 mm cuvette and, unless indicated, after 10 minutes of deoxygenation with N_2. The sample temperature was controlled through a refrigerating circulator bath thermostat (Huber MPC-K6) coupled to the sample holder. The emission spectra were recorded with a custom-made spectrofluorometer where an Andor ICCD camera is coupled to a spectrograph. Each temperature-dependent spectrum was recorded with 50 ns of delay with respect to the excitation laser pulse to avoid registering the scattering signal and using a power density of 30 mW/cm^2. Each emission spectrum was acquired thirty times to average over possible laser intensity oscillations. The emission decays at the maxima of PtOEP phosphorescence band (λ = 647 nm) and DPA upconverted emission (λ = 433 nm) were recorded using a Hamamatsu photomultiplier, an Infiniium Agilent Technologies oscilloscope and a power density of 30 mW/cm^2. 10 acquisitions were obtained for each decay and averaged to increase the signal-to-noise ratio. Threshold excitation intensities (I_{th}) and UC quantum yields (Φ_{UC}) were determined using a cw green laser (Z-laser, 532 nm, 18 mW, 0.07 cm^2). I_{th} were obtained by measuring the integrated UC intensities at each power density used to irradiate the sample. The PtOEP-DPA solutions for the I_{th} threshold determination were prepared at concentrations able to guarantee measurable UC in a wide range of power densities (see Supporting Information). UC quantum yields (Φ_{UC}) were determined by means of the following equation:[27]

$$\Phi_{UC} = \Phi_r \frac{A_r\, F_s\, I_r\, \eta_s^2}{A_s\, F_r\, I_s\, \eta_r^2} \quad (1)$$

In this equation, Φ_r is the fluorescence quantum yield of the standard selected, F_s and F_r are the integrated emission intensities measured for the sample and the standard, A_s and A_r are the optical densities of the sample and the standard at the excitation wavelength, I_s and I_r are the excitation intensities employed, and η_s and η_r are the refractive indices of the solvents used. As standard sample, we took liquid and solid solutions of *N,N'*-bis(*sec*-butyl)-1,6,7,12-tetra-(4-*tert*-butylphenoxy)perylene-3,4:9,10-tetracarboxylic diimide (PTDI) in hexadecane and eicosane, whose fluorescence quantum yields were previously determined to be 1.0 by comparison with a room-temperature chloroform solution of PTDI ($\Phi_{fl,PTDI}$ = 1.0).[43] In this way we assured that the sample of interest and the reference were in the same media and state (solid or liquid) during the (Φ_{UC}) determination. It must be noticed that using equation 5 and the standard selected in this work, a maximum value of Φ_{UC} = 0.5 can be obtained, since 2 absorbed photons by the donor are required to generate 1 upconverted fluorescence photon from the acceptor.

Digital photos and video. Digital photographs and the video of the colors emitted by the samples at different temperatures were collected with a photocamera, placing in front of the objective a band-cutting filter (transmittance below 1% between 500 and 600 nm) to eliminate the green excitation light scattering.

RESULTS AND DISCUSSION

Thermal UC switching in hexadecane. In a first step we selected *n*-hexadecane as phase change material, since it can dissolve the dyes of choice to achieve TTA-UC and it presents a relatively sharp phase transition, a high boiling point, and a melting point close to room temperature (T_m = 291 K).[44] PtOEP and DPA were chosen as highly absorbing triplet sensitizer and emitter, respectively. The former displays absorption maxima at 380, 500 and 535 nm and emission around 645 nm in toluene, while DPA fluorescence is centered at 433 nm and only shows small overlap with PtOEP absorption bands (Supporting Information, Figure S1).[13, 45] Diluted HD solutions (~μM) of PtOEP and DPA were then prepared at different concentrations (see Experimental Section for more details) and we measured their emission spectra below and above HD melting point (λ_{exc} = 532 nm, N_2 atmosphere).

When the PtOEP-DPA solution in HD was irradiated at 303 K (i.e. above T_m), both UC (λ_{max} = 433 nm) and phosphorescence (λ_{max} = 647 nm) emissions were detected, which demonstrated incomplete energy transfer from the sensitizers to the emitters in the liquid phase (Figure 1a). Surprisingly, the UC process was enhanced upon cooling the sample below T_m (273 K), which led to the freezing of the medium and hence hampered molecular diffusion. Instead of inhibiting TTA-UC by preventing TTET and TTA processes, the liquid-to-solid phase transition resulted in a significant and unforeseen increase of the UC fluorescence at expense of the phosphorescence emission (Figures 1a and S2). This phenomenon was found to be reversible and the starting emission profile was completely recovered once the initial temperature (303 K) was restored (Figure S3).

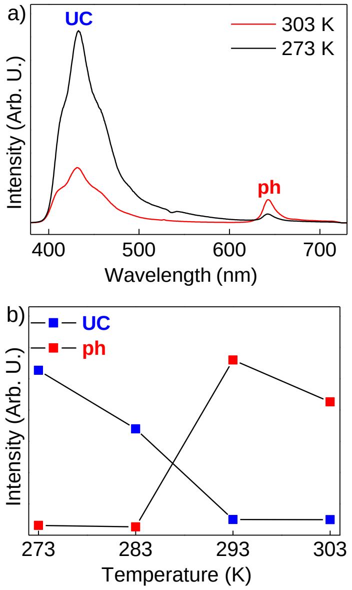

Figure 1. a) Emission spectra of a PtOEP-DPA mixture in HD solution at different temperatures ([PtOEP] = 10 μM; [DPA] = 300 μM). b) Thermal variation of the UC and phosphorescence (ph) integrated intensities for a different HD solution of PtOEP-DPA ([PtOEP] = 1 μM; [DPA] = 30 μM).

Lowering dyes concentration in the HD solution by one order of magnitude (PtOEP] = 1 μM; [DPA] = 30 μM) did not only allow preserving this unexpected thermal behavior, but permitted reversible switching from nearly pure phosphorescence to nearly pure UC emission upon temperature variation (Figure S4). As shown in Figure 1b, this occurred abruptly in a narrow thermal range (~20 K) and around the T_m of HD. Thus, while very minor intensity variations arising from temperature effects on sensitizer ISC yield and/or solvent viscosity were observed away from the solvent melting point (e.g. from 293 to 303), sudden suppression of red luminescence (18-fold intensity decrease) and growth of UC emission (10-fold intensity increase) were clearly observed when converting the liquid HD solution into a frozen solid matrix.

As far as we know, this intriguing temperature-dependent emission behavior had not been previously reported and, indeed, it reveals completely opposite performance to what is expected and has been observed in other media such as liposomes,[40] polymers,[41] and liquid donor-acceptor mixtures.[42] Namely, liquid-to-solid transition in a mixture of sensitizers and emitters does favor TTA-UC instead of inhibiting this energy transfer-based phenomenon. As such, an additional mechanism other than molecular diffusion, should account for the strong UC luminescence observed in frozen PtOEP-DPA HD solutions. Several alternative factors were considered to rationalize this behavior. On the one hand, it could not be attributed to a thermal increase in the fluorescence quantum yield (Φ_{fl}) of the emitter, since the variation in Φ_{fl}

reported for DPA when cooling from 298 to 190 K (+12%)[46] cannot explain the 250-900% enhancement in UC signal observed in our measurements.

Another plausible argument to rationalize our results could be differential oxygen solubilities and/or diffusivities in HD liquid and solid phases, as recently described for a gel system.[37] However, we discarded this explanation on the basis of two additional experiments. First, only dim phosphorescence (and no UC signal) was detected for both liquid and solid HD solutions under aerated conditions, thus demonstrating high O_2 solubility and diffusivity in both cases (Figure S5). Second, to assess the effect of residual oxygen molecules present in the deaerated mixtures where UC emission was detected, temperature-dependent PtOEP triplet lifetimes (τ_T) were determined from phosphorescence decay measurements under N_2 atmosphere in DPA-free solutions (Figure 2).

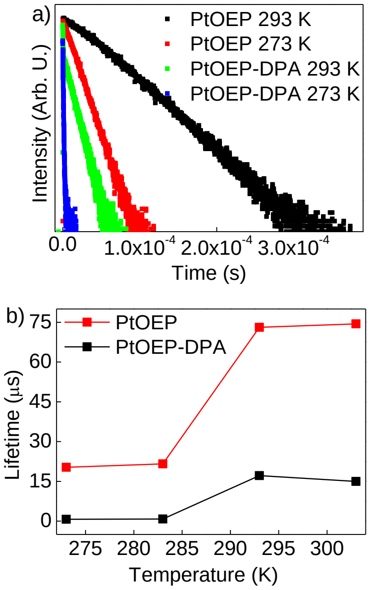

Figure 2. a) Phosphorescence decays at λ = 647 nm of deaerated HD solutions of PtOEP ([PtOEP] = 1 μM) and PtOEP-DPA ([PtOEP] = 1 μM; [DPA] = 30 μM) measured at 293 K and 273 K. b) τ_T values determined from the phosphorescence decays registered for these PtOEP and PtOEP-DPA samples at different temperatures.

Little τ_T variations were measured once above or below HD melting point in these experiments. By contrast, large lifetime variations were observed upon phase change, a 3.6-fold lifetime drop (from 73 μs at 293 K to 20 μs at 273 K) being determined when freezing. Notably, this result is completely the opposite of what should be expected in the case that UC enhancement in solid HD arose from lower oxygen quenching effects, since a concomitant increase in PtOEP τ_T should have been measured.

Instead, the significant decrement of the lifetime upon matrix solidification was ascribed to PtOEP aggregation in the solid samples.[47] Fine inspection of the phosphorescence spectra of liquid and solid PtOEP solutions in HD (Figure S6) allowed a new emission band at $\lambda \sim 770$ nm to be identified upon crystallization, which is consistent with the formation porphyrin aggregates.[48, 49] However, the contribution of this band to the overall spectrum is rather small and further studies are in progress to deeply investigate the nature and the role of the PtOEP aggregates.

A similar situation is expected to occur in DPA-containing HD samples, for which the intensity of the excitonic PtOEP aggregate emission band at $\lambda \sim 770$ nm was also found to be rather minor (Figure S7) and no clear excitonic absorption band was observed (Figure S8), neither at higher PtOEP concentrations (10 μM). On the other hand, while little PtOEP τ_T variations were measured once above or below HD melting point, dramatic triplet lifetime changes were again encountered across its T_m in the presence of DPA. It must be noted that τ_T decreased both in the liquid and solid state upon DPA addition, as expected due to the occurrence of sensitizer-emitter TTET (Figure 2). However, a much larger DPA quenching effect was observed in the frozen HD sample (29-fold decrease in τ_T, corresponding to TTET quantum yield $\Phi^{273}_{TTET} = 0.97$) with respect to the liquid solution (4.3-fold decrease in τ_T, $\Phi^{293}_{TTET} = 0.77$). As consequence, an enormous PtOEP triplet lifetime decrement took place during phase change (from 17 μs at 293 K to 0.7 μs at 273 K), which suggests a clear enhancement of the donor-acceptor interaction in the solid sample, where normally the molecular diffusion and collisions are reduced.

These results can only be explained on the basis of the formation of mixed aggregates where sensitizer and emitter molecules are arranged randomly but at suitable distances (< 1 nm)[13-14,19-21] to enable efficient energy transfer. The dye aggregation in solid HD was ascribed to low solubility in the chosen aliphatic solvent. Actually, PtOEP and DPA self-assembly in materials with high aliphatic content[37,42] and the high affinity of DPA π-rich aggregates towards PtOEP have been already reported.[37] Hence, we suggest that mixed sensitizer-emitter molecular aggregates are formed in our case by cooling below HD T_m, thus ensuring the very short interchromophoric distances required for the energy transfer processes involved in TTA-UC.[13-14,19-21] This enables upconverted emission to be largely boosted in the solid phase even when starting from very diluted PtOEP-DPA HD solutions where diffusion-controlled UC is disfavoured by low dye concentrations and high solvent viscosity. Although aggregation effects were very recently described to account for upconversion when using matrix free UC liquids,[42] and donor-acceptor chromophores specially designed to supramolecularly interact,[50] or by controlling the triplet energy of the dye sensitizers through formation of aggregates in the solid state (aggregation-induced photon upconversion),[51] to our knowledge, this constitutes the first report of UC enhancement through thermally-induced switchable chromophore aggregate formation.

To better evaluate the aggregation-induced enhancement of the UC emission of PtOEP-DPA mixtures in HD, we measured the change of the threshold excitation intensity upon solvent solidification. I_{th}, a critical parameter characterizing the performance of photon upconverting systems, sets the minimum excitation power density at which maximum UC quantum yield is obtained and it corresponds to the excitation intensity at which a quadratic-to-linear transition is observed in the UC emission power dependence.[52] As shown in Figure S9, clearly different I_{th} values were determined for liquid (I_{th} = 82 mW/cm^2) and solid (I_{th} = 37 mW/cm^2) HD samples with [PtOEP] = 10 μM and [DPA] = 300 μM). In particular, a 2.2-fold decrease in threshold excitation intensity was observed upon HD freezing, thus further proving the higher efficiency of the UC process in the solid matrix with respect to the liquid solution. In particular, a maximum value of Φ_{UC} = 0.060 was registered for the solid sample at excitation power densities above I_{th} = 37 mW/cm^2. Noticeably, similar Φ_{UC} and I_{th} values were measured in non-viscous liquid toluene solutions of PtOEP-DPA mixtures at higher dye concentrations (Φ_{UC} = 0.077 and I_{th} = 18 mW/cm^2 for [PtOEP] = 15 μM and [DPA] = 500 μM in toluene at room temperature[53]), which confirms the UC enhancement effect achieved by HD solidification.

Several effects deriving from solvent crystallization and concomitant dye aggregation could account for such an enhancement. As already discussed above, formation of mixed PtOEP-DPA assemblies in solid HD resulted in a 25% increase in triplet-triplet energy transfer from donors to acceptors, one of the intermolecular processes involved in upconversion. Additionally, the triplet-triplet annihilation process between acceptor molecules could also benefit from solvent freezing, either by increasing the intrinsic lifetime of DPA triplet state in the resulting solid matrices or by enhancing the efficiency of intermolecular TTA due to the short inter-chromophoric distances in the aggregates. Time-resolved analysis of the UC emission,[54] however, demonstrated that the unimolecular decay rate constant of DPA triplet state (k^{T}_{DPA}) remained nearly unaltered with temperature in the 293-273 K range (Figure S10), thus ruling out a significant enhancement of DPA triplet state population by HD solidification. Instead, a clear increase in the bimolecular rate constant characterizing the TTA process (k_{TTA}) was estimated[55] to occur upon dye aggregation on the basis of the I_{th}, Φ_{TTET} and k^{T}_{DPA} values determined for the liquid and solid PtOEP-DPA samples in HD ($k^{273\,K}_{TTA}$ / $k^{293\,K}_{TTA}$ ~ 1.8, see the Supporting Information). This further confirms that such temperature-induced aggregation mechanism is responsible for the enhancement of interchromophoric interactions in solid HD matrices and, as such, of the concomitant increase in UC emission observed in the solid phase. By properly tuning the dyes pair concentration, this eventually allows accomplishing nearly complete transition from red phosphorescence to blue upconverted fluorescence upon freezing. Notably, this new temperature-dependent emitting system based on phase-change materials is simple and quite versatile to be easily extended to other dyes or media reaching different working conditions (temperature or optical windows).

UC switching in a room-temperature solid phase change material. Once developed this new strategy towards thermally switchable UC emission, the next step was proving that it could be extended to other phase-change materials with different melting points. For this we chose eicosane (EC), a 20-carbon aliphatic compound, since it is chemically similar to HD and has a melting point slightly above room temperature (T_m = 310 K),[56] which could then be exploited to achieve aggregation-induced UC emission in the solid state without requiring cooling.

The spectral behavior of EC solutions of PtOEP-DPA were thus studied above and below T_m. Upon optimization of dyes concentration, a similar thermal response to that found in HD was registered. In this case, however, the switching temperature was observed around 310 K, and 13-fold UC emission enhancement and 12-fold phosphorescence emission decrease were measured upon liquid-to-solid transition of EC (Figure 3). Such a UC enhancement was confirmed by measuring the threshold excitation intensities below and above EC melting point (Figure S11), since a lower value was determined in the solid phase (I_{th} = 47 mW/cm^2) with respect to the liquid solution (I_{th} = 88 mW/cm^2). Actually, Φ_{UC} values as high as 0.059 were registered above I_{th} = 47 mW/cm^2 for the solid EC sample, which are similar to those obtained in solution at higher PtOEP and DPA concentrations.[53]

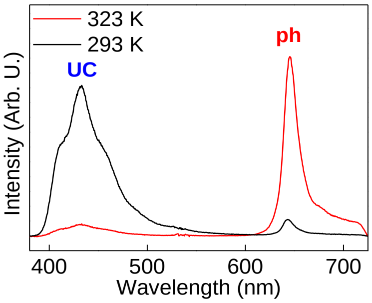

Figure 3. Emission spectra of a PtOEP-DPA mixture in EC at different temperatures ([PtOEP] = 1 μM; [DPA] = 30 μM).

The temperature-dependent phosphorescence decay study for the PtOEP-DPA pair in EC gave analogous results to those described above for HD solutions (Figure S12), with sensitizer τ_T largely dropping (from 30 to 2.2 μs) upon solvent solidification and, therefore, demonstrating chromophore aggregation and enhanced intermolecular interaction (Φ^{313}_{TTET} = 0.68, Φ^{303}_{TTET} = 0.92). As observed in HD samples, most of these aggregates in solid EC should be formed by disordered, weakly interacting dye molecules, since only small contribution in the absorption (at λ ~ 555 nm, Figure S13) and emission (at λ ~ 760 nm) spectra arising from strongly coupled PtOEP aggregates were measured in both DPA-free (Figure S14) and DPA (Figure S15) containing mixtures. Further studies devoted to elucidate the nature and role of aggregate species are in progress. However, this aggregation process seemed to be very efficient, since UC emission in solid EC could be reached at even lower PtOEP concentrations (0.1 μM, Figure S16). Once again, this proved that, even though molecular collisions were highly unlikely in the solid state due to the reduced mobility of the molecules in frozen EC, the interchomophoric interaction processes and, as such, UC emission were still more favored than in the liquid phase by increasing the local dye concentration in the aggregates formed. In addition, repetitive heating-cooling cycles showed complete reversibility of the phosphorescence-to-UC conversion with no detrimental effect on the intensities registered, thus indicating an excellent stability of the switching system (Figure 4a).

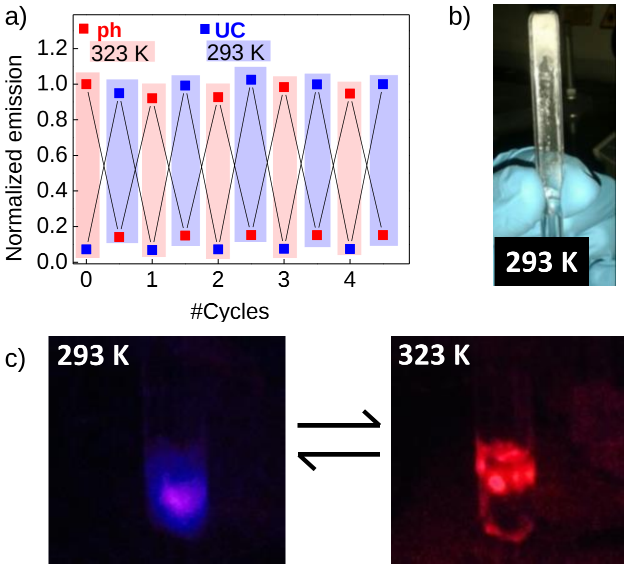

Figure 4. a) Repetitive UC and phosphorescence emission switching by thermally cycling this sample between 293 K and 323 K. b) Solid EC matrix containing PtOEP-DPA UC pair. c) Digital photographs of the emission resulting from a PtOEP-DPA EC solution at 293 K and 323 K.

An important consequence of using EC as solvent is that, given its higher melting point, we were able to achieve a solid material exhibiting upconverted luminescence at room temperature (Figure 4b-c, S17 and video). This is not a very common situation for TTA-UC systems relying on intermolecular energy transfer processes, which require either complex designs where chromophore interaction is preserved in the solid state (e.g. gels,[37] liquid-filled capsules,[22-24,57-58] rubber polymer matrices,[19,41,59]or chromophore-functionalized polymers[60-61]) or very high dye concentrations in simpler systems (e.g. high T_g polymers[19,62-63], solvent-free sensitizer-emitter solid[47] or liquid[42]mixtures). While our approach matches the structural and preparation simplicity of the latter, it allows UC emission to be observed at dye concentrations at least 3 orders of magnitude lower, thus involving very little material consumption (below the μM level). To corroborate this, poly(methyl methacrylate) films were prepared with the same PtOEP-DPA concentrations routinely used in our HD or EC samples ([PtOEP] = 1 μM; [DPA] = 30 μM). No UC fluorescence was observed at room temperature, but just red phosphorescence due to large mean separation between the randomly dispersed chromophores in the polymer matrix (Figure S18). This is in contrast to the selective dye aggregation achieved in our solid HD or EC samples, which is crucial to enable UC.

Thermal UC switching with other organic dyes. After proving that the switching temperature could be tuned by simply replacing the phase-change solvent, we investigated other TTA-UC pairs in EC. In particular, we tested other emitters with different molecular structures and triplet energies while preserving the same porphyrin sensitizer (Figure S19): 1,3,6,8-tetraphenylpyrene and 9,10-dimethylanthracene.

As expected, when both diluted sensitizer-emitter mixtures were irradiated at 323 K in liquid EC, phosphorescence at 650 nm was essentially observed (Figure 5). Temperature decrease across EC melting point then produced reversible 130-fold (λ_{max} = 440 nm) and 34-fold (λ_{max} = 430 nm) UC enhancements and simultaneous phosphorescence quenching in the PtOEP-TPPy and PtOEP-DMA systems, respectively. This demonstrates the versatility and broad scope of the aggregation-induced strategy developed in this work towards solid and thermally-switchable TTA-UC materials.

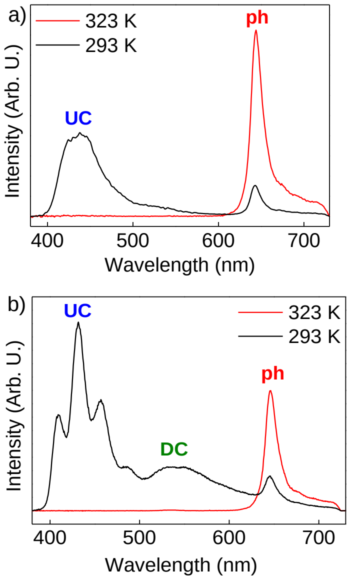

Figure 5. a) Emission spectra of a PtOEP-TPPy mixture in EC at different temperatures ([PtOEP] = 0.1 μM; [TPPy] = 100 μM). b) Emission spectra of a PtOEP-DMA mixture in EC at different temperatures ([PtOEP] = 1 μM; [DMA] = 30 μM).

Interestingly, the PtOEP-DMA pair in solid EC also revealed another broad emission band in the visible spectral region (λ_{max} = 526 nm, Figure 4b). It originated from downconverted (DC) DMA excimer emission,[64] another intermolecular photophysical process that was previously exploited to produce white-light emitting solutions from TTA-UC systems.[13,28] It is worth to note that DC emission is normally observed in highly concentrated DMA solutions (90 mM).[28] In our case, however, it was registered in the solid phase and at much lower concentrations (30 μM), which therefore further demonstrates the occurrence of dye aggregation in the solid phase change medium. More importantly, this makes our solid dyes pair matrices novel materials capable to produce both UC and DC emissions with low chromophore content based on selective chromophore aggregation.

CONCLUSION

In the present work we developed a versatile and straightforward method to obtain temperature-switchable molecular emitting systems based on upconversion. Our strategy does not require complex designs involving the use of additional functional compounds, but it simply consists in the preparation of dilute mixtures of sensitizer-emitter pairs in phase change materials where they present low solubility. This leads to selective dye aggregation upon phase change, which largely enhances chromophore interaction and, as such, upconverted luminescence in the solid state. In this way, nearly complete, sudden and reversible switching between red sensitizer phosphorescence and blue emitter UC fluorescence is achieved around the liquid-to-solid transition of the system, whose thermal and spectral response can be finely tuned upon variation of the solvent and dyes of choice. Furthermore, this allows upconversion to be observed in molecular solid materials at room temperature using simpler constructs and up to 1000 times less dye concentrations than the best examples reported to date, thus opening new avenues for the development of functional UC-based devices.

ASSOCIATED CONTENT

Supporting Information.

Dye chemical structures, absorption and fluorescence spectra of DPA and PtOEP dyes in toluene and of DPA-PtOEP mixtures in liquid and solid HD and EC solutions, time dependent phosphorescence and UC emission decays, temperature dependent UC emission intensities, power dependent UC emission intensities for I_{th} determination, UC and phosphorescence emission in air atmosphere, emission of PtOEP/DPA in PMMA, sequence of pictures showing the color change of the phase-change emitting material upon temperature variation. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

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Notes

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ABBREVIATIONS

TTET, triplet-triplet energy transfer; TTA, triplet-triplet annihilation; NIR, Near InfraRed; UC, upconversion;DC, downconverted; ph, phosphorescence; HD, *n*-hexadecane; EC, eicosane; PtOEP2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine platinum(II); DPA, 9,10-diphenylanthracene; TPPy, 1,3,6,8-tetraphenylpyrene; DMA, 9,10-dimethylanthracene; T_m, melting point; T_g, glass transition temperature; Φ_{fl}, fluorescent quantum Yield.

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