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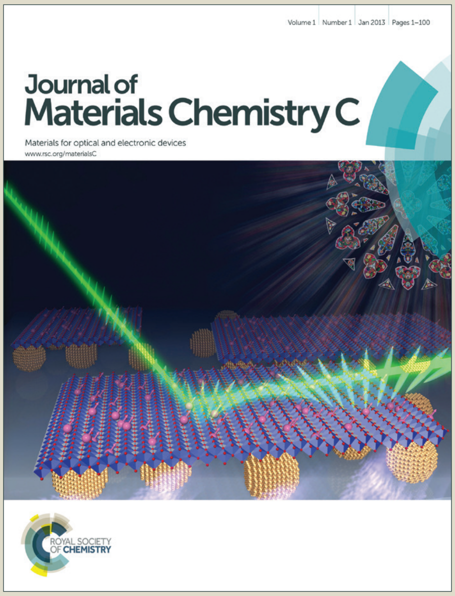

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Highly Efficient Photochemical Upconversion in a Quasi-Solid Organogel

Kabilan Sripathy,[a] Rowan W. MacQueen,[a] Joshua Peterson,[a] Yuen Yap Cheng,[a] Miroslav Dvořák,[b] Dane R. McCamey[c] Neil D. Treat,[d] Natalie Stingelin[d] and Timothy W. Schmidt*[a]

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Despite the promise of photochemical upconversion as a means to extend the light-harvesting capabilities of a range of photovoltaic solar energy conversion devices, it remains a challenge to create efficient, solid state upconverting materials. Until now, a material has yet to be found which is as efficient as a liquid composition. Here, a gelated photochemical upconversion material is reported with a performance indistinguishable from an otherwise identical liquid composition. The sensitizer phosphorescence lifetime, Stern-Volmer quenching constants and upconversion performance (6% under one-sun illumination) were all found to be unchanged in a quasi-solid gelated sample when compared to the liquid sample. The result paves the way to a new family of efficient photochemical upconversion materials comprised of macroscopically solid, but microscopically liquid gel, for application in photovoltaics and photocatalytic water-splitting.

1 Introduction

Photochemical upconversion has the potential to increase light-harvesting efficiencies of quantum solar energy convertors.[1] But, the most efficient systems to date are liquids, which are inherently incompatible with large-scale device fabrication processes. All solids reported thus far have demonstrated reduced performance. Here we demonstrate a solid, in the form of an organogel, with identical performance to the corresponding liquid.

In recent years, photochemical upconversion (PUC) has emerged as an efficient strategy to convert light of lower energy into higher energy, with applications as diverse as photovoltaics,[1–4] water splitting,[5,6] bioimaging[7] and oxygen sensing[8]. There are two main approaches to upconvert incoherent light: exploitation of atomic-like transitions in rare-earth ions;[9–12] or PUC, where energy storage in triplet states is coupled to subsequent triplet-triplet annihilation (TTA) in organic molecules.[1,13–16] Of the two, the latter offers the spectral versatility and relatively high efficiency required for application.[17–20]

Much effort in PUC research has so far concentrated on photovoltaic applications,[1] where upconversion is employed to harvest sub-bandgap light and re-radiate at a photon energy above the bandgap. If this can be done efficiently, then the Shockley-Queisser limit,[21] which applies to single threshold solar cells, can be surpassed,[22] and much higher energy-harvesting efficiencies can be obtained. Indeed, upconversion is calculated to best serve solar cells with bandgaps in the 1.7 eV range,[23,24] which corresponds well with lead methylammonium halide perovskite solar cells, recently shown to be very promising solar energy harvesting materials.[25]

TTA-based UC requires two different chemical species, a sensitiser and an emitter. The sensitizer is designed to absorb photons and rapidly intersystem-cross to a nearby triplet state. The emitter collects these triplet states by Dexter energy transfer,[26] and combines the energy of two photons by triplet-triplet annihilation. The energy transfer processes required to bring about PUC are illustrated in Fig. 1.

As TTA and triplet energy transfer (TET) are Dexter-type mechanisms occurring only when chemical species are in close proximity,[26,27] a key requirement for high efficiency PUC is triplet mobility. As a result, the most efficient compositions thus far investigated are liquid phase.[28] However, the robust encapsulation of organic liquids presents a major engineering problem. Liquids flow and evaporate, leading to seals being dissolved and broken. This drastically limits the range of applications for which the materials are suitable.

A solid upconvertor would be ideal for device engineering,[14] but solid state upconverters thus far reported lack the triplet mobility crucial for high efficiency. Most approaches followed for creating solid-state PUC materials have involved the blending of the sensitizer and emitter species into a photophysically benign polymeric host matrix, which serves as a

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[a] *School of Chemistry, UNSW Sydney, NSW 2052, Australia. Tel: +61 439 386 109; E-mail: timothy.schmidt@unsw.edu.au*

[b] *School of Chemistry, The University of Sydney, NSW 2006, Australia.*

[c] *School of Physics, UNSW Sydney, NSW 2052, Australia.*

[d] *Department of Materials and Centre for Plastic Electronics, Imperial College, London SW7 2AZ, UK.*

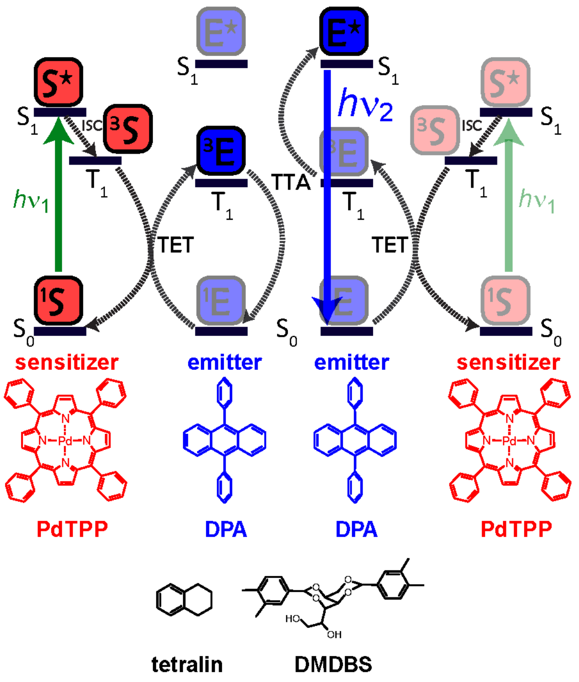

Fig. 1 The energy transfer steps involved in the PUC process. Sensitizer molecules absorb low energy photons, $h\nu_1$ and undergo intersystem crossing (ISC) to the T_1 state. The triplet energy is transfered to emitter molecules (triplet energy transfer, TET) which then undergo triplet-triplet annihilation (TTA) to bring about a singlet excited emitter molecule which emits a higher energy photon, $h\nu_2$. The structures of the photochemically active compounds (PdTPP/DPA), solvent (tetralin) and gelator (DMDBS) used in this study are shown below.

mechanical support for the chromophores. Due to the need for triplet mobility, it has been found that a matrix material with a low glass-transition temperature is desirable.[5,29] Consequently, many of the systems reported thus far are based on soft ‘rubbery’ polymers.

PUC has been demonstrated in host materials as diverse as cellulose acetate,[30] polystyrene,[31] a copolymer of ethyleneoxide and epichlorohydrin,[29,32] polyurethane,[33,34] and poly-butylacrylate.[5] Furthermore, upconverting nanoparticles can be created with different polymeric host media, including polystyrene[35] or poly-butylacrylate.[36] Aggregation and phase-segregation of the dye species are serious issues which are partially responsible for the low efficencies demonstrated by solid upconvertors compared to liquid systems.[14] Employment of a polymer host, which takes on the emitter role, doped with a sensitizer species, has been investigated, including porphyrin-doped polyfluorene,[17] porphyrin-doped poly-pentaphenylene,[37] and porphyrin-doped “super yellow”.[38] But aggregation of the porphyrin triplet sensitizers, and trapping of emitter triplets, appear to be a major problems.

The work of Monguzzi and coworkers is especially notable, for they directly compare the performance of a solution of diphenylanthracene and platinumoctaethylporphyrin in butylacrylate polymer, and in the corresponding monomer solution.[5] The quantum yield of the polymer matrix is found to be always lower than that of the solution sample, irrespective of irradiation intensity, due to the reduced molecular mobility in the polymer environment. The difference in efficiency is more than a factor of two under solar-equivalent irradiance, and under the strong annihilation regime the polymer lags in efficiency due to inefficient quenching of sensitizer triplet states.

What is desirable is a material that is microscopically liquid while macroscopically solid, affording the advantages of both phases in the relevant spatial domains. Svagan et al. recently demonstrated a “synthetic leaf” which was capable of upconversion by virtue of sensitizer and emitter materials being dissolved in cellulose nanoparticles with oily cores.[39] But, their material demonstrated significant sensitizer phosphorescence, indicating inefficent triplet energy transfer. This is possibly due to the high viscosity of the oil employed (hexadecane, 3.03 mPa s at 25 °C[40]). Kang and Reichmanis followed a similar approach,[41] creating polymer capsules with liquid cores. However, much lower efficiencies were observed, compared to a corresponding DMF solution, on account of the very viscous liquid medium necessitated by the polymerization strategy (60 mPa s compared to 0.92 mPa s for DMF).

Here we show that efficiencies indistinguishable from the solution phase can be obtained in a gel – a liquid trapped through numerous microscopic interconnected domains. A gel is a macroscopically highly viscous substance that will retain its shape and fail to flow when inverted. But, providing the liquid domains are larger than the length scale of the PUC process, the macroscopic viscosity of the gel is not expected to impede the photochemical reaction.

1,3:2,4-bis(3,4-dimethylbenzylidene) sorbitol (DMDBS) is a well-studied organogelator,[42] which self-associates below a certain temperature to form a fibrillar network that gels the host solvent.[43,44] It is used to nucleate polymer crystallization in functional materials, including organic photovoltaics,[45] and has been used to create a *quasi*-solid state dye-sensitized solar cell, a system which relies on rapid molecular diffusion.[46] In this contribution we show that an upconvertor composition gelated with DMDBS is indistinguishable, in all measures of performance, from the liquid sample. As such, it is shown that liquid upconvertors can be made macroscopically solid without impeding upconvertor performance.

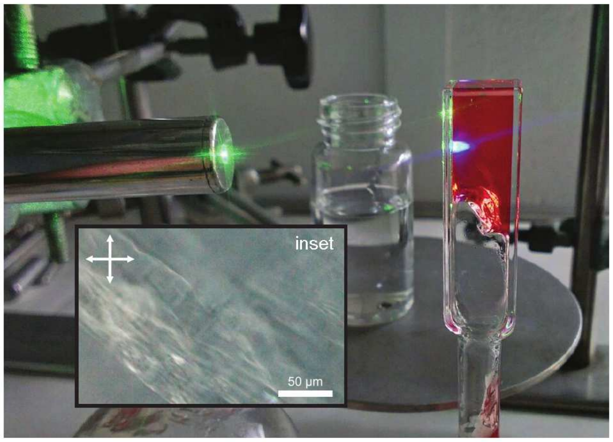

Fig. 2 A photograph of a gelated material performing green-to-blue upconversion in an inverted cuvette. A half-filled vial of water is shown for orientation. Inset: a cross-polarized transmission optical microscope image of the PUC gel.

2 Results and Discussion

2.1 Gelated Upconvertor

The produced PUC gel consists of DMDBS as the organogelator, tetralin as the solvent, and PdTPP and DPA as the upconversion active materials. Formation of the gel first requires the formation of a homogeneous solution, which is achieved through heating at 120°C, effectively dissolving the DMDBS in the PUC solution. Upon cooling to room temperature, the solution undergoes a thermoreversible transition from a liquid to a gel. The gelation mechanism relies on the nucleation and crystallization of the DMDBS within the blend; this crystallization process forms high aspect-ratio nano- and microscopic features of DMDBS that entangle, producing interactions that cooperatively inhibit macroscopic rotation/translation and result in the formation of a *physical gel*. Conceptually, the structure of a physical gel is ideally suited for upconversion because it is a macroscopically solid material with a high volume fraction of interstitial space occupied by the solvent, permitting unimpeded diffusion of the upconversion active materials between the entanglements.

Figure 2 shows the macroscopically solid PUC gel, a salmon-coloured material held in an inverted vacuum cuvette. A hand-held 532 nm laser pointer irradiates the material, and blue light, the result of PUC, can be seen emanating from the gel. The inset of Fig. 2 is a cross-polarized transmission optical microscope image of the PUC gel, the observed contrast within the image arising from the birefringence of the gel. This reveals that the material is composed of bundles of DMDBS fibrils, hundreds of micrometers in length, that transverse the focal plane of the image, signifying a 3-dimensional microstructure. Importantly, the incorporation of the upconversion active materials has little influence on the formation of the physical gel; cross-polarized transmission optical microscope images show indistinguishable properties between the neat gel and gel containing the upconversion active materials.

Table 1 Kinetic parameters for phosphorescence quenching of PdTPP by DPA in liquid and gel phases.

	liquid	gel
[PdTTP] (mM)	0.005	0.005
k_{SV} ($\times 10^5$M^{-1})	1.121(10)	1.140(27)
τ_0 (μs)	662(5)	663(8)
k_q ($\times 10^8$M^{-1}s^{-1})	1.686(20)	1.72(5)

2.2 Stern-Volmer Plot

Stern-Volmer quenching of PdTTP phosphorescence by DPA is shown in Fig. 3, plotted as open symbols. The quenching constants, $\sim 1.1 \times 10^5$ M^{-1} are identical within the stated error, and thus it appears that the gel does not hinder the bimolecular quenching of PdTPP triplet states by DPA. The phosphorescence lifetimes were likewise found to be identical within error, yielding a bimolecular quenching rate constant of $k_q = 1.7 \times 10^8$ M^{-1}s^{-1}. This is quite low, but the viscosity of tetralin is some 3.4 times higher than toluene. As such, a rate of $k_q = 6 \times 10^8$ M^{-1}s^{-1} would be expected in toluene, which is closer to the 10^9 M^{-1}s^{-1} benchmark usually observed in solution.[47] Kinetic parameters derived from Fig. 3 are given in Table 1.

2.3 Triplet Energy Transfer Efficiency

Plotted as solid symbols in Fig. 3 are the triplet energy transfer efficiencies, Φ_{TET}, as a function of DPA concentration. Near-quantitative quenching of the PdTPP triplets is achieved with just 0.5 mM of DPA, on account of the long triplet lifetime of PdTTP (660 μs), and reasonable bimolecular rate constant.

Both samples exhibit identical phosphorescence lifetimes and quenching characteristics, ensuring identical DPA triplet concentrations under identical illumination. Providing that subsequent TTA kinetics is also identical between samples, then the upconversion efficiency should be, also.

2.4 Upconversion Action Spectroscopy

The emission spectra of DPA in the gelated and liquid samples are identical. Upconversion action spectra are plotted in Fig. 4. The spectra plot the linear response of emitter fluorescence to a monochromatic, chopped probe beam under continuous pumping conditions of a known solar equivalence. The porphyrin Q-band is clearly visible in the green region centred at

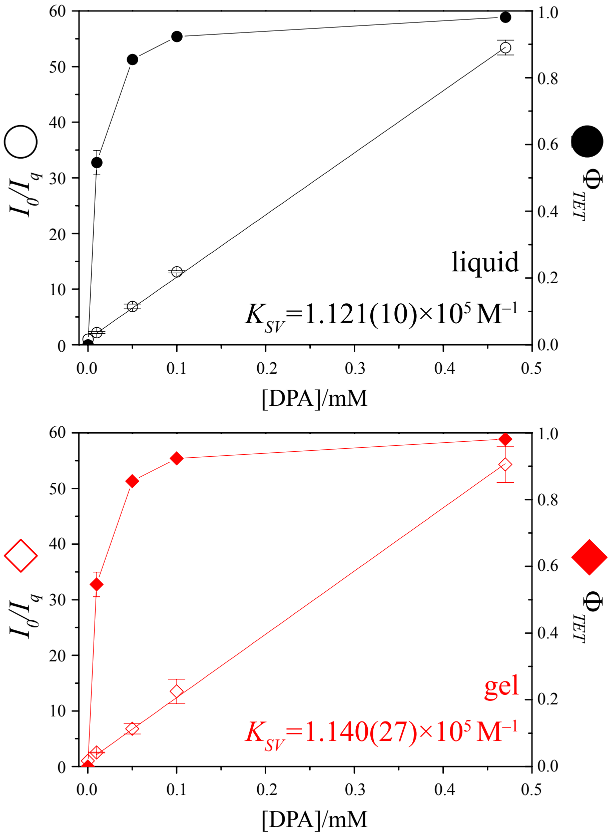

Fig. 3 Stern-Volmer plots of phosphorescence quenching in liquid (top) and gel (bottom). The quenching constants are indistinguishable. As judged by $\Phi_{TET} = 1 - I_q/I_0$, both samples are nearly fully quenched at $[\mathrm{DPA}] = 0.5\,\mathrm{mM}$.

525 nm. Light of this wavelength is converted into detectable blue DPA fluorescence at an efficiency 0.08 that of direct excitation of DPA at 400 nm. Since PUC can at best achieve a quantum efficiency of 0.5, this represents 16% of maximum. But, such an estimate ignores the details of the light absorption profiles and reabsorption of emitted fluorescence. These effects have been incorporated into a detailed model which can be found in MacQueen *et al.*[48]. The model is described by the equation

$$f(\lambda) = A\left[\frac{\alpha_p^e(\lambda)}{\alpha_p(\lambda)+\alpha_{pl}} + \Phi_{TTA}\frac{\alpha_p^s(\lambda)}{\alpha_p(\lambda)+\alpha_b+\alpha_{pl}}\right], \qquad (1)$$

where α_p^e and α_p^s are the extinction coefficients at the probe wavelength due to emitter and sensitizer respectively, and α_{pl} and α_b are the extinction coefficients at the detection and bias wavelengths. Equation 1 is plotted as a solid line in Fig. 4 for both the gelated and liquid PUC compositions. The only free parameters in the model are A, an overall scale factor, and

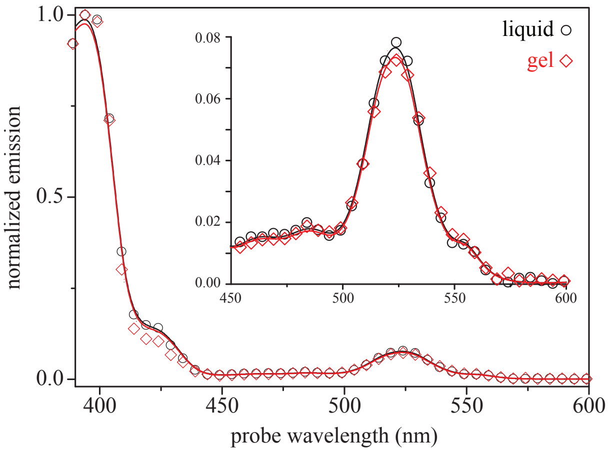

Fig. 4 Upconversion excitation spectra of the gelated and liquid upconversion compositions under 3 sun equivalent excitation. They are nearly identical, with the PdTPP Q-band clearly present. Details of the apparatus can be found in MacQueen *et al.*[48].

Φ_{TTA}, the yield of excited singlet states from pairs of triplets, with all other terms being determined from measured absorption spectra. The close agreement of Equation 1 with our data is highly satisfactory.

2.5 Triplet-Triplet Annihilation Efficiency

From the fitting, the salient parameter Φ_{TTA} is extracted, which for the spectrum plotted in Fig. 4 is > 0.14. The Φ_{TTA} value extracted from illumination equivalent to $0-3.2$ suns is plotted in Fig. 5. The gelated and liquid samples are again identical. The efficiencies are seen to climb with irradiance with slightly sub-linear behaviour, indicating a tendency towards saturation. The behaviour may be modelled, assuming a steady state DPA triplet concentration,

$$\frac{d[^3\mathrm{DPA}]}{dt} = 0 = k_\phi[\mathrm{PdTPP}] - k_1[^3\mathrm{DPA}] - k_2[^3\mathrm{DPA}]^2, \qquad (2)$$

where k_ϕ is the rate of photon absorption by the sensitizer species, and k_1 and k_2 are the first and second-order decay constants respectively.

Solving for $[^3\mathrm{DPA}]$,

$$[^3\mathrm{DPA}] = \frac{-k_1 + \sqrt{k_1^2 + 4k_2k_\phi[\mathrm{PdTPP}]}}{2k_2} \qquad (3)$$

The TTA efficiency is the proportion of triplets decaying by second-order means, f_2, multiplied by the efficiency that the second order decay events yield excited singlet emitters, η_c.

$$\Phi_{TTA} = f_2\eta_c = \frac{k_2[^3\mathrm{DPA}]}{k_1 + k_2[^3\mathrm{DPA}]}\eta_c \qquad (4)$$

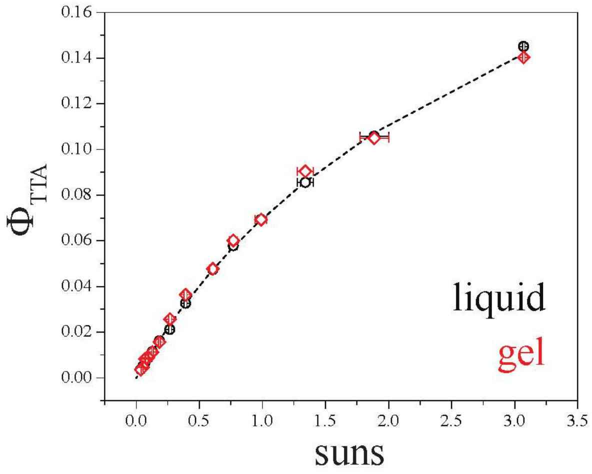

Fig. 5 The TTA efficiency as a function of effective solar flux for the best-performing liquid and gel samples. The are indistinguishable. The dashed line is a model described in the text which predicts a maximum Φ_{TTA} of 0.45.

Fitting this model to the data points in Fig. 5 predicts a maximum efficiency of $\Phi_{TTA} = \eta_c = 0.45$. The maximum quantum efficiency of the upconvertor is then $\Phi_{UC} = \Phi_{TTA}\Phi_F/2$, which in this case will be about 0.2, assuming a high fluorescence quantum efficiency. These numbers agree very well with the maximum efficiency values observed by Monguzzi and co-workers, who observed a plateau under high irradiance of $\Phi_{UC} = 0.22$ for a DPA upconvertor in solution.[5]

2.6 Diffusion

The diffusion of triplets, following generation at the origin, is taken to follow Fick's law, but with an additional term due to their first order decay

$$\frac{\partial\phi(\mathbf{r},t)}{\partial t} = D\nabla^2\phi(\mathbf{r},t) - k_1\phi(\mathbf{r},t) + s\delta(\mathbf{r})\delta(t). \qquad (5)$$

With a source of triplets represented by a sensitizer molecule, then the above equation can be solved,

$$\phi(\mathbf{r},t) = \frac{s}{(4\pi Dt)^{3/2}}\exp\left(-\frac{|\mathbf{r}|^2}{4Dt} - k_1 t\right). \qquad (6)$$

When the above equation is integrated in time, one arrives at the steady-state distribution about a continuous source,

$$\int dt\phi(\mathbf{r},t) \propto \frac{\exp\left(-\sqrt{\frac{k_1}{D}}r\right)}{r} \qquad (7)$$

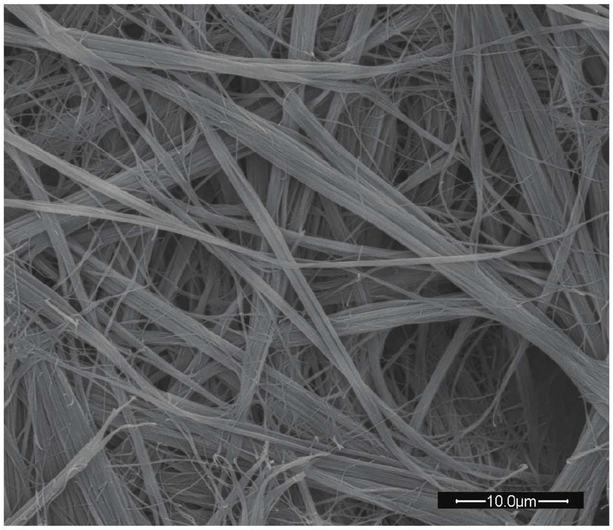

Fig. 6 Scanning electron micrograph of the dried DMDBS gel, showing cavities greater than 1 μm.

We may estimate the diffusion distance at time τ in the usual way from

$$\bar{r} = \sqrt{4D\tau}. \qquad (8)$$

From the Stokes-Einstein relation,

$$D = \frac{k_B T}{6\pi\eta R}, \qquad (9)$$

where R is the radius of the diffusing particle. For a particle of radius 0.5 nm, a diffusion coefficient of 2×10^{-10} m^{2}s^{-1} may be inferred in tetralin, which has a viscosity of 2.02 mPa s. Thus, the average distance a triplet molecule diffuses in a typical 100 μs lifetime is 300 nm. Providing the gel contains liquid cavities larger than this scale, then triplets will mostly not encounter a gel fibril within their lifetime, and the photochemistry should proceed as per the liquid.

Further evidence of the gel structure within the liquid is provided by the optical and SEM micrographs presented in Fig. 2 and 6, respectively. As noted above, the inset in Fig. 2 evidences a 3-dimensional network of fibrils, hundreds of microns in length. Figure 6 shows an SEM image of a dried sample of the gel. It can be seen that the gel fibrils are several μm thick, but also exhibit cavities of size much larger than this. It may be expected that the solvent between the fibrils behaves microscopically much as it would in the absence of the gel, and as such the upconversion system presently investigated would also behave, kinetically, as it would in the absence of the gel. Thus, we attribute the high upconversion efficiencies obtained herein to the non-interference of the gel structure with the diffusional kinetics of the photochemically

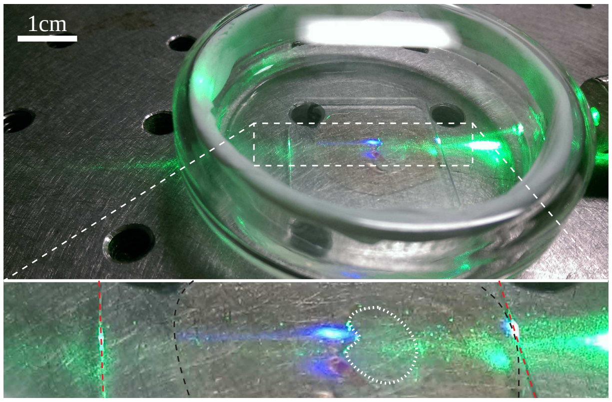

Fig. 7 Photograph of a glass slide spin-coated with PUC organogel. The slide is submersed in an oxygen-scavenging water layer. Inset: When 532 nm light is applied to the slide (white outline), PUC is clearly visible along the path of the laser in the region covered by the film (surrounded by the black dashed line). A patch of the gel layer has also been removed (dotted white outline), and UC light is not visible in this region.

active components of the gel. It can be expected that diffusion of the sensitizer/emitter can be thereby controlled by the extent to which the solvent is gelled. The organogel is not itself impermeable to oxygen, and will require further encapsulation for operation under atmospheric conditions. However, the ability to encapsulate films of oxygen-sensitive materials is well-established in the organic photovoltaics field.[49]

2.7 Encapsulation

To demonstrate the suitability of the PUC gel for device applications, we applied a layer of the material to a glass substrate via a standard fabrication technique, namely spin-coating. The DMDBS-PUC mixture was heated to 130°C in a pipette, and applied to a preheated glass substrate. The substrate was immediately spun at 500 RPM for 10 seconds, resulting in a film 120 μm thick, as determined by absorbance. When the film is subjected to anoxic conditions (in this case, by submersing it within an oxygen-scavenging aqueous layer), illumination with 532 nm light provides a clear demonstration of upconversion, as shown in Fig. 7. Other fabrication methods, such as Gravure (doctor blade) printing, should also be possible with gel-based PUCs.

2.8 Application to Photovoltaics

We have previously reported many applications of liquid upconvertors to thin-film solar cells including amorphous silicon (a-Si:H) and dye-sensitized cells.[2–4,50,51] Application of the present gel-phase upconvertor is therefore immediately possible, and we expect that the results will be identical to the comparable liquid solution. For application to a-Si:H or DSCs, we have previously employed a red-absorbing sensitizer, such as tetrakisquinoxalinoporphyrin palladium (II), and an orange-emitter, namely rubrene.[2–4,50,51]

Further, the efficiency of the present system could be improved by employing a lower viscosity solvent. We used tetralin, because its boiling point was such that it made safely achieving the temperature required, for dissolution of the gelator, rather facile. However, its viscosity is more than three times that of toluene. Ethylbenzene (0.63 mPa s) and *meta*-xylene (0.58 mPa s) have viscosities close to toluene (0.56 mPa s), while exhibiting boiling points exceeding 130 °C.[40] As such, they may prove to be preferable to tetralin.

The gel should be photostable under continuous illumination with the low energy photons available behind a semi-transparent solar cell. Since the DMDBS is transparent to visible light, it does not exhibit excited electronic states below 3.0 eV, and as such is expected to be immune to the effects of low energy visible or near infrared photons. The photodegradation of the photochemically active components has not been studied in detail, but a preliminary study may be found in Schulze and Schmidt[1].

3 Conclusions

It has been demonstrated that gelation of an organic solvent with DMDBS can lead to a solid upconvertor without impinging on the diffusional kinetics of the chromophoric components. As a consequence, for the PdTPP:DPA couple, identical phosphorescence lifetimes, Stern- Volmer quenching and upconversion efficiency was determined for gelated and liquid samples, indicating that the bimolecular kinetics of both samples are identical. A Φ_{TTA} value of 0.07 was determined under one-sun pumping, despite the high viscosity of the tetralin solvent as compared to toluene. The utility and ease of handling of the solid gel sample comes from retaining the efficiency of a liquid solution but with versatility in the degree of gelation and, consequently, controllable mechanical stability. This material composition paves the way for widespread employment in the many applications of photochemical upconversion.

4 Methods

4.1 Chemical Preparation

Palladium tetraphenylporphyrin (PdTPP, Frontier Scientific) and 9,10-diphenylanthracene (DPA, Sigma-Aldrich) were employed as the sensitiser and emitter respectively, dissolved in tetralin (Sigma-Aldrich). For Stern-Volmer plots, the PdTPP concentration was 0.005 mM. For upconversion efficiency measurements, the concentrations were [PdTPP] = 0.5 mM and [DPA] = 10 mM. Gelation was achieved by adding 0.3% w/v 1,3:2,4-Bis(3,4-dimethylbenzylidene) sorbitol (DMDBS, Hangzhou Dayangchem) to the PUC solution, heating to approximately 120° C and subsequently cooling to room temperature. All samples were degassed in a custom-built vacuum cuvette through several freeze-pump-thaw cycles, to remove oxygen.

Vacuum-degassing a DMDBS organo-gel is a long and inefficient process, so all solvated samples were degassed before gelation, which required heating the solution under vacuum ($10^{-3} - 10^{-4}$ mBar) to 120° C. As such, toluene, our usual solvent of choice, was determined to be too volatile. For this reason, we favoured tetralin, despite its higher viscosity, which has a higher boiling point.

4.2 Optical Measurements

Phosphorescence lifetimes were obtained using an electronically gated intensified CCD camera mounted to a spectrograph (Princeton). The sensitizers were excited using the $\sim$ 5 ns pulse of a frequency-doubled Q-switched Nd:YAG laser (Quantel).

The Stern-Volmer plots were made by measuring phosphorescence excitation spectra, of samples prepared with various concentrations of DPA, using a home-built front-face excitation spectrometer.[48] The excitation spectra were integrated to yield the data points for the Stern-Volmer plots.

Upconversion excitation spectra were obtained using the same apparatus as for the phosphorescence excitation spectra. However, as the measurement is performed with a chopped perturbative probe and lock-in amplification, what is obtained is the linear response to the probe light. Since upconversion is a non-linear process at low light levels,[52–54] the measurements were performed with a continuous bias which pumped the sensitizer molecules at a rate equivalent to a level of solar concentration (suns), where one sun is 1000 $\mathrm{W m^{-2}}$ of the AM1.5G spectrum. Details of this apparatus can be found in MacQueen *et al.*[48].

SEM of the dried gel was obtained using the FEI Quanta 200, of the Mark Wainwright Analytical Centre, in high vacuum mode.

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