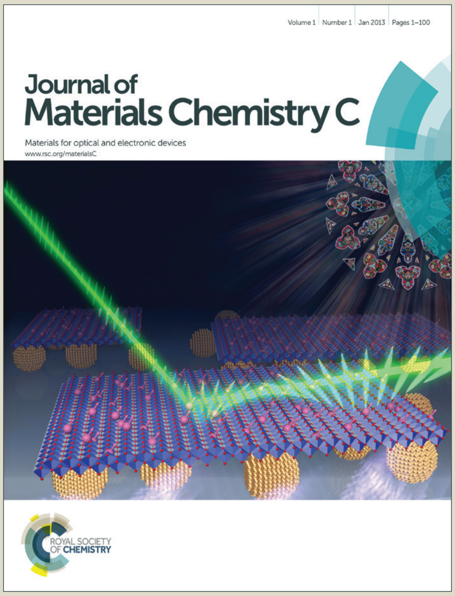
Journal of Materials Chemistry C

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/materialsC

Journal of Materials Chemistry C RSCPublishing

COMMUNICATION

Low-Power Photon Upconversion in Organic Glasses

Cite this: DOI: 10.1039/x0xx00000x

Roberto Vadrucci, Christoph Weder* and Yoan C. Simon*

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Green-to-blue upconverting molecular glasses consisting of a metal octaethylporphyrin (MOEP, M = Pd, Pt) sensitizer and 9-(4-hydroxymethylphenyl)-10-phenyl anthracene (DPA-CH_2OH) as emitter are reported. In these materials, incident light is transformed into higher-energy radiation by way of triplet-triplet annihilation upconversion. The DPA-CH_2OH/ MOEP mixtures form transparent glasses when cooled from the thermally stable melt, even at rates as low as 1 °C/min. In a systematic study the PdOEP concentration was varied from 0.025 to 6.6 mol%. The normalized upconverted light intensity decreased with increasing sensitizer concentration by almost three orders of magnitude, as a result of sensitizer aggregation. The upconverted light intensity also decreased upon deliberate crystallization of the upconverting materials. Beyond demonstrating first embodiments of upconversion in molecular glasses, the results highlight the importance of morphology control in solid-state upconverting materials.

The upconversion of low-intensity light by triplet-triplet annihilation is useful for many applications that range from solar harvesting to bio-imaging[1] to soft actuators.[2] This process has long been known to occur in solutions of sensitizer-emitter pairs that support a specific cascade of photophysical events, but could only recently be realized in solid, mostly polymeric, materials. Here, we report a new class of upconverting materials based on molecular organic glasses.

Triplet-triplet annihilation upconversion (TTA-UC) is a process in which the energy of two incident photons is combined and re-emitted as blue-shifted light. This effect can be achieved with chromophore systems composed of a sensitizer and an emitter. The former absorbs light, undergoes intersystem crossing to a triplet excited state, followed by energy transfer to the emitter. Two excited emitter species then form an encounter complex and eventually annihilate, leading to delayed fluorescence. Since its discovery[3,4] the TTA-UC effect was demonstrated for many chromophore pairs in solution,[1] including palladium or platinum octaethylporphyrin (PdOEP, PtOEP) and 9,10-diphenylanthracene (DPA) (Fig. 1 and 2).[5] PdOEP and PtOEP are attractive sensitizers because they offer a high extinction coefficient at the porphyrin Q-band (λ_{max} = 536, 546 nm, respectively), a transparency window between Q-and Soret-bands (<400 nm), and high phosphorescence quantum yield (Fig. 1).[6] TTA-UC has only recently been demonstrated in rubbery[7-10] and glassy[11-13] polymers. The high translational mobility of chromophores in rubbery matrices leads to efficient TTA-UC at low chromophore content, but cooling the polymer below its glass transition temperature (T_g) suppresses the UC, due to restriction of the various diffusion-controlled energy transfer steps.[8]

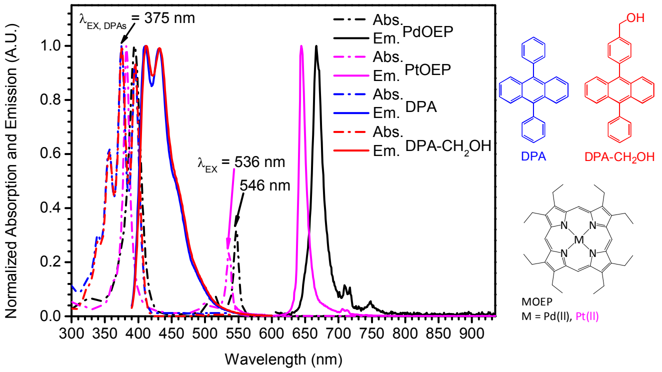
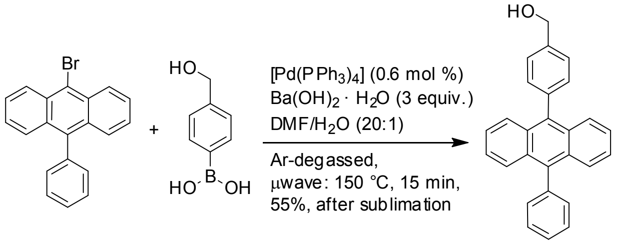


Fig. 1 Normalized absorption and emission spectra of 9,10-diphenylanthracene (DPA), 9-(4-hydroxymethylphenyl)-10-phenyl anthracene (DPA-CH_2OH), PdOEP and PtOEP in toluene (c=10^{-5} M). Emission spectra were recorded with excitation at 375 (DPA and DPA-CH_2OH), 536 (PtOEP) and 546 nm (PdOEP).

This limitation can be overcome by increasing the chromophore content, so that chromophore-chromophore distances are below the Dexter energy transfer radii.[14,15] This approach was used to achieve TTA-UC in rigid polymer matrices,[11,13] and sensitizer-doped emitter nanowires and nanoparticles.[16,17] Other strategies to enable UC in polymers are the confinement of chromophores in (nano)particles,[18,19] soft/liquid core – hard shell assemblies,[20-22] nanostructured films,[23] or embedding the sensitizer into a polymeric emitter.[24,25] The latter approach is interesting, as the chromophore content is maximized and the emitter-sensitizer distance is minimized. However, an attempt to co-crystallize PdOEP and DPA showed that phase segregation[26] and the formation of PdOEP aggregates stifled the UC process in this system, reflecting that co-crystallization is generally difficult to predict and control.[27] Surprisingly, there has been, to the best of our knowledge, no attempt to embed the sensitizer in a glassy matrix formed by a low-molecular organic emitter.

Thus, we here present PdOEP-doped DPA-based molecular glasses (MGs) as first embodiment of a novel design strategy for organic UC materials. These solids consist of the chromophores only and display a homogeneous phase, where the disordered emitter serves as the solvent for the sensitizer. MGs can be melt-processed into complex shapes and display less light-scattering than crystalline materials.[28]

With the objective to create an analogue of DPA that crystallizes less readily, the new 9-(4-hydroxymethylphenyl)-10-phenyl anthracene (DPA-CH_2OH) was synthesized by the microwave-assisted Suzuki-Miyaura cross-coupling of 9-bromo-10-phenyl anthracene and 4-(hydroxymethyl) phenylboronic acid (Scheme 1) and isolated in 55% yield after sublimation.



Scheme 1. Microwave-assisted Suzuki-Miyaura synthesis of DPA-CH_2OH

DPA-CH_2OH was characterized by NMR spectroscopy, mass spectrometry and elemental analysis, and displays optical absorption and emission spectra that are virtually identical to those of DPA (Fig. 1). The thermal properties of DPA-CH_2OH and DPA were analyzed by differential scanning calorimetry (DSC). The first heating scan of as-prepared DPA-CH_2OH shows a melting point, T_{m1}, of 218°C (Fig. 2a), slightly lower than that of DPA (T_{m1} = 251°C, Supplementary Fig. S1, S8-S9) and much lower than that of 9,10-di(4-hydroxymethylphenyl) anthracene (DPA-$(CH_2OH)_2$, T_{m1} > 300°C), which was also investigated (Supplementary Scheme S1, Fig. S1, S10), but shows thermal decomposition below T_m. The first DSC cooling scan of melted DPA-CH_2OH (Fig. 2a, cooling rate = 5ºC/min) does not show any crystallization peak, while the second heating scan (Fig. 2a) displays a T_g around 77˚C, an exothermic transition around 139˚C (associated with the crystallization of the sample, T_c), and a melting transition at 219˚C (T_{m2}), which matches that of the original material. Powder X-ray diffraction patterns (Fig. 2b) of the as-prepared DPA-CH_2OH show well-defined reflections, while heated and quenched samples display diffuse diffraction. Thus, these experiments demonstrate that DPA-CH_2OH solidifies from the melt as an amorphous glass with a T_g of around 77˚C, even if cooled at a rate of only 5°C/min (Fig. 2 and Supplementary Fig. S9). This behavior contrasts with that of DPA, which crystallizes even when cooled at a rate of 50°C/min.

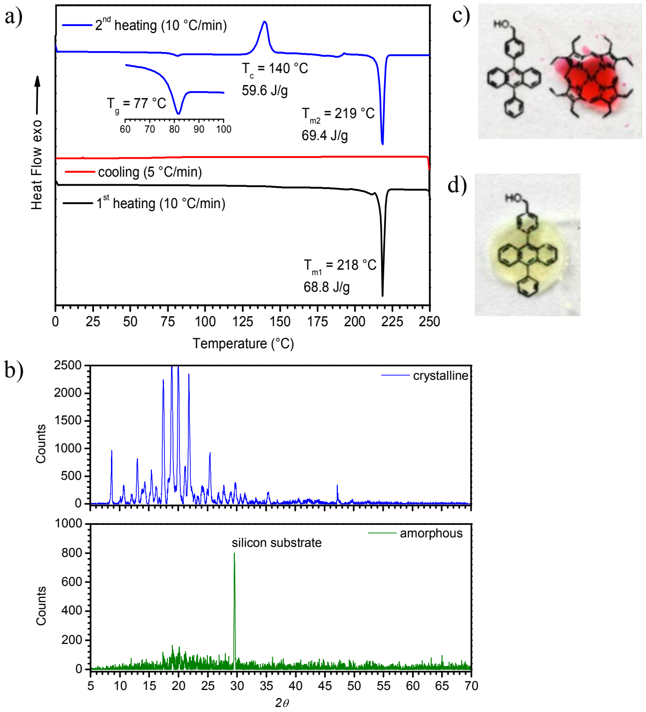


Fig. 2 a) DSC traces (first heating, cooling, second heating and magnification of the regime between 60 and 100 ºC in the second heating scan) of as-prepared DPA-CH_2OH. Heating and cooling rates, as well as the enthalpies of the various transitions are indicated in the graph. b) Powder X-ray diffractograms of as prepared ("crystalline", top) and heated and quenched ("amorphous", bottom) DPA-CH_2OH. c) Picture of DPA-CH_2OH MG doped with 0.7 mol% PdOEP. d) Picture of DPA-CH_2OH MG without sensitizer.

In view of its glass forming ability, DPA-CH_2OH was utilized as a host for metal-containing sensitizers to create UC-MGs. All chromophores utilized display sufficient thermal stability to permit melt-processing at 250°C (Supplementary Table S1, Supplementary Fig. S8-11). DPA-CH_2OH and PdOEP or PtOEP were pre-mixed by dissolution in CH_2Cl_2 and evaporation of the solvent; the concentrations of the emitter was varied between 6.6 and $7{\bullet}10^{-3}$ mol% (*vide infra*). The mixtures were placed between glass slides, the assemblies were placed under an inert atmosphere, heated to melt the chromophore mixtures, and rapidly cooled to quench the melts into homogeneous transparent glasses (Fig. 2c-d, see Supplementary Information for experimental details). First, the characteristics of neat and PdOEP-doped DPA-CH_2OH (0.025 mol% PdOEP) were compared, varying the cooling rate from 1 to 50°C/min. None of the DSC cooling traces (acquired after heating the sample to 250°C) show a crystallization peak upon cooling (Supplementary Fig. S9a and S14a). The traces of the 2nd heating cycle display the transitions associated with a MG (T_g, T_c, T_{m2}, Supplementary Fig. S9b and S14b), and reveal similar crystallization enthalpies. In the case of the neat DPA-CH_2OH, the second heating traces of samples that were previously cooled at rates between 5 and 50°C/min are identical. The DSC trace of the sample that was cooled at a rate of 1°C/min also shows small melting and crystallization peaks around 193°C and 195°C, which are attributed to a different polymorph (Supplementary Fig. S9). These peaks are also visible in the second heating traces of DPA-CH_2OH doped with 0.025 mol% PdOEP cooled before at rates between 1 and 10°C/min (Supplementary Fig. S14), but absent when cooled faster. Here, the magnitude of the melting peak at 193°C increases with decreasing cooling rate, and, at the same time, the temperature of the main crystallization peak decreases from ~139 to ~135˚C. Taken together, these data indicate the formation of MGs at all cooling rates and compositions, but slow quenching, in particular upon incorporation of PdOEP, appears to support the formation of nucleation sites for a DPA-CH_2OH polymorph. This result suggests that PdOEP may aggregate at low cooling rates. Therefore, MGs prepared for UC experiments were cooled as quickly as possible and the influence of the cooling rate on the UC intensity of PdOEP-doped DPA-CH_2OH was investigated in detail (*vide infra*).

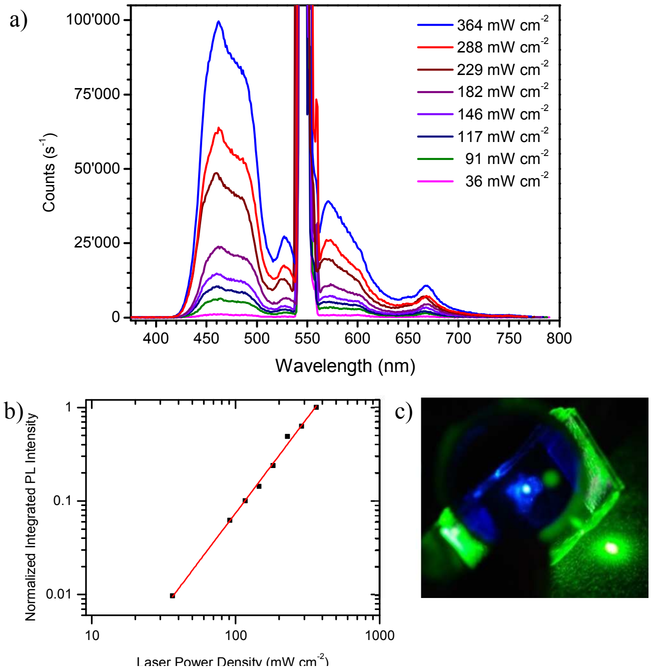


Fig. 3 a) Emission spectra of a DPA-CH_2OH MG doped with 0.07 mol% PdOEP, acquired upon irradiation with a 2 mW green HeNe laser (543 nm), whose power density was varied with the help of neutral density filters as indicated in the figure. b) Double logarithmic plot of the normalized integrated upconverted emission intensity as function of incident power (36-364 mW cm^{-2}). A linear regression (red line) reveals a quadratic relation (exponent = 2.04 +/- 0.05). A double linear representation is shown in Supplementary Fig. S15c . c) Picture of a MG containing 0.025 mol% PdOEP irradiated with 2 mW green HeNe laser. The blue fluorescence originates from TTA-UC and is observable through a 500 nm short pass filter alongside with reflected laser light.

All PdOEP-doped MGs displayed detectable upconversion when exposed to the green light of a HeNe laser at 543 nm, even at excitation power densities as low as 36 mW cm^{-2} (Fig. 3). Neat DPA-CH_2OH MGs do not show any UC under identical conditions. Direct excitation of the undoped MG at 395 nm leads to slightly red-shifted emission and higher fluorescence intensity compared to undoped, crystalline DPA-CH_2OH powder (Supplementary Fig. S20b). The upconverted emission spectra of the PdOEP-doped DPA-CH_2OH MG show the characteristic features of DPA-CH_2OH emission (Fig. 3a and Supplementary Fig. S15). For MGs containing 0.07 mol% (Fig. 3a) and 0.025 mol% PdOEP (Supplementary Fig. S15), the power densities were varied. The normalized integrated upconverted emission increased with the incident power density in the regime of 36 – 364 mW cm^{-2} in quadratic manner (Fig. 3b).[26] Comparable UC intensities were measured under air and nitrogen (Supplementary Fig. S19). In addition, signals centered around 560 - 620 nm can be observed in all PdOEP-doped upconverting MGs when excited at 543 nm. The intensity of these red-shifted signals relative to the upconverted emission was especially high at the two highest PdOEP concentrations, where PdOEP phosphorescence at 665 nm and a signal at 650 nm were also observed (Supplementary Fig. S16 and S18). Together with the observation that the PdOEP-doped DPA-CH_2OH phase segregates at the highest sensitizer concentration (6.6 mol%) (Supplementary Fig. S17), we attribute the red-shifted emission to the formation of PdOEP aggregates. While the use of a glassy material mitigated the aggregation of the porphyrin moieties, it did not completely suppress it. Blank *et al.* recently proposed that triplet-triplet fusion in neat PtOEP-films leads to the population of higher energy states laying between the lowest triplet state and double the energy of the lowest triplet state rather than to radiationless decay.[29]

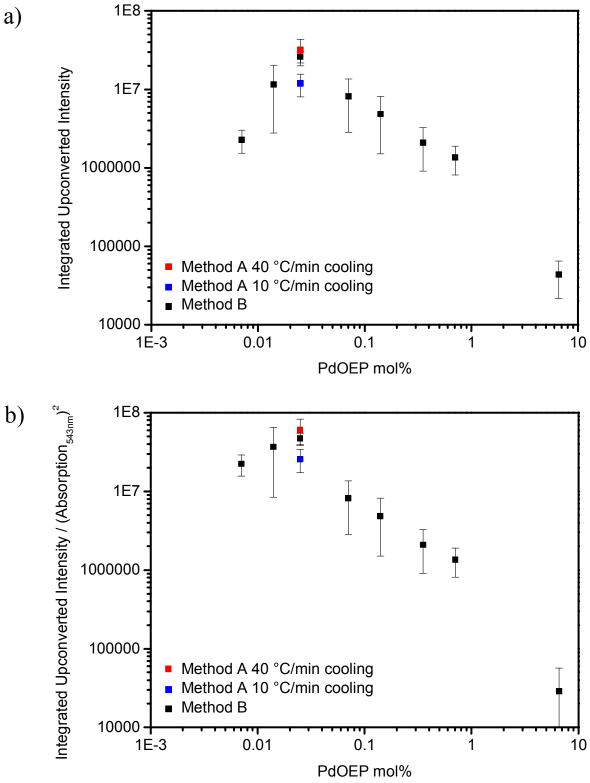


Fig. 4 Integrated upconverted intensity of PdOEP-doped DPA-CH_2OH MGs as a function of the sensitizer content. a) Integrated upconverted intensity as measured. b) Integrated upconverted intensity normalized by division through the squared absorbance at 543 nm (irradiation wavelength).

Noting that comparatively low upconverted emission intensity could be observed for DPA-CH_2OH doped with 6.6 mol% PdOEP, the TTA-UC intensity of MGs was investigated as a function of PdOEP content. Fig. 4a shows that the UC intensity decreases by almost three orders of magnitude when the PdOEP content was increased from 0.025 to 6.6 mol%; MGs with a PdOEP content of <0.025 mol% also exhibit a lower upconverted intensity than the latter composition. The same trend is seen if the data are normalized for the absorption of the samples (Fig. 4b). This result is consistent with growing PdOEP aggregation as its concentration increases.

Based on the above results, the influence of the cooling rate on the UC intensity of MGs with 0.025 mol% PdOEP was investigated. Cooling the melt from 250°C to 25°C at a rate of 10°C/min (see Supplementary Information for experimental details, Method A) afforded MGs with a lower UC intensity than samples that were quenched with a cooling rate of 40°C/min (red and blue squares in Fig. 4, and Supplementary Fig. S18). The MG-UC intensity of the latter was comparable with that of samples prepared by Method B (black squares in Fig. 4, Section 7 in the Supplementary Information), showing that the methods are interchangeable. Method B, which permitted higher sample throughput, was therefore applied routinely in this study. As demonstrated in the thermal characterization studies (*vide supra*), faster cooling rates limit PdOEP aggregation and support the results obtained with the DSC using the same composition (Supplementary Fig. S14, *vide supra*).

The new materials provide an opportunity to study the same chromophore composition in samples of different morphology. Thus, the emission profiles of (i) PdOEP-doped DPA-CH_2OH MGs (Fig. 5), (ii) PtOEP-doped DPA-CH_2OH MGs (Supplementary Fig. S12 and S13), (iii) thermally crystallized MGs, and (iv) MOEP/DPA-CH_2OH solvent-premixed solids were compared upon excitation at 543 nm. To crystallize the MGs (iii), MGs (i) or (ii) were heated to 145°C for 165 min, i.e. above the crystallization temperature of DPA-CH_2OH (140°C). For a given composition (0.025 mol% PdOEP), MGs (i) displayed a strongly enhanced green to blue UC compared to crystallized MGs (iii) and solvent-mixed solids (iv) (Fig. 5). This finding clearly demonstrates that morphology plays a crucial role in UC efficiencies in the solid state. We primarily attribute this observation to the limited efficiency of energy transfer across boundaries in polycrystalline materials and porphyrin aggregation. Additionally, several other factors can also reduce the efficiency in powders such as diffraction and increased oxygen quenching due to higher surface area.

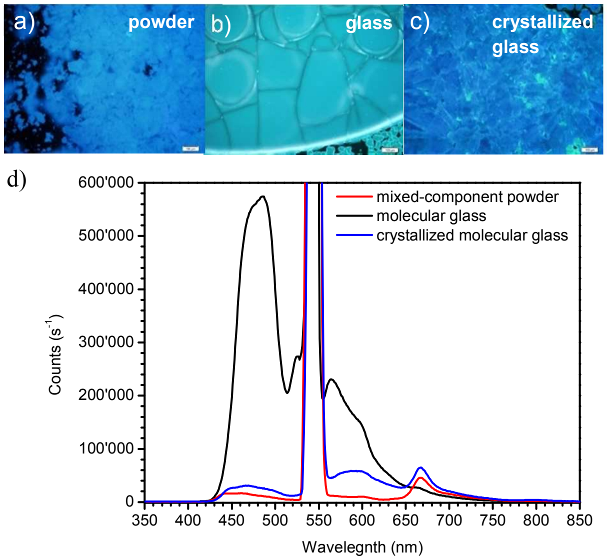


Fig. 5 a)-c) Optical fluorescence microscope images of DPA-CH_2OH doped with 0.025 mol% of PdOEP: a) premixed solid, b) MG (film edge) and c) crystallized MG. d) Fluorescence emission spectra of samples a)-c) when irradiated with 2 mW 543 nm green HeNe laser.

PtOEP was used as an additional sensitizer because of its characteristic emission at 756 nm upon aggregation.[30] The electronic states associated with this transition lay lower than the lowest triplet state of DPA (1.64 vs. 1.78 eV),[15] making the transfer from PtOEP aggregates to DPA energetically unfavorable. PtOEP can therefore serve as a probe to monitor aggregation. For MGs (ii) containing 0.025 mol% PtOEP, the UC far exceeded that of crystalline samples (iii) and (iv) of the same composition. The MGs (ii) displayed a broad laser red-shifted emission different from those of crystallized MGs (iii) (0.025 and 0.7 mol% PtOEP, Supplementary Fig. S12 and S13). The latter displayed two main red shifted signals: PtOEP phosphorescence (λ_{max} = 649 nm) and the aggregate-specific emission at λ_{max} = 756 nm,[30] which was more pronounced at higher PtOEP concentrations and led to lower UC intensity (6.7 vs 63 kcounts/s at λ_{max} = 468 nm). The original postulate that sensitizer aggregation is detrimental to TTA-UC is therefore verified by these results.[24] A comparison of the relative ratio of upconverted light to red-shifted signals of MGs (i) and (ii) (Fig. 5 and Supplementary Fig. S12) further suggests that the former exhibits proportionally higher upconversion intensity. This observation and the more intricate laser-red shifted emission profiles in PdOEP-doped glasses at 0.7 mol% MOEP are attributed to the considerably longer phosphorescence lifetime of PdOEP compared to PtOEP (650 µs and 85 µs, respectively),[30,31] leaving more time for alternative relaxation processes to happen.

Conclusions

In summary, the current work presents the first examples of low-power TTA-UC in molecular glasses. 9-(4-Hydroxymethylphenyl)-10-phenyl anthracene can readily be quenched into a glassy state by undercooling. Transparent MGs based on DPA-CH_2OH and PdOEP or PtOEP are easily fabricated and exhibit striking green-to-blue upconversion. In these materials, the upconversion intensity was shown to be much more intense than in crystalline materials of the same composition. A quadratic relationship to the incident light intensity and strong dependence on the sensitizer concentration were observed. Porphyrin aggregation at high concentrations is believed to be detrimental for UC efficiency; however, the solubility may be improved by appropriate chemical derivatization of the sensitizer. Molecular glass-based upconverting materials appear to be highly suitable to further explore the complex photophysical processes of TTA-UC in the amorphous, disordered state,[32] and the design approach presented here is general and should be readily applicable to other (appropriately derivatized) UC-chromophore pairs.

Acknowledgements

The authors are grateful for the financial support of the Swiss National Foundation SNF (project number 135405) and the Adolphe Merkle Foundation. We thank Prof. Dr. Bernard Grobéty, University of Fribourg, for recording powder X-ray diffraction spectra and assistance with the interpretation of the data.

Notes and references

Adolphe Merkle Institute, University of Fribourg, Rte de l'Ancienne Papeterie, CH-1723 Marly 1, Switzerland.
E-Mail: yoan.simon@unifr.ch; christoph.weder@unifr.ch.

† Electronic Supplementary Information (ESI) available: Synthetic procedures and characterization, DSC and TGA data, preparation and characterization of doped and undoped molecular glass films. See DOI: 10.1039/c000000x/

1. Y. C. Simon and C. Weder, *J. Mater. Chem.*, 2012, **22**, 20817-20830.
2. Z. Jiang, M. Xu, F. Li and Y. Yu, *J. Am. Chem. Soc.*, 2013, **135**, 16446-16453.
3. C. A. Parker and C. G. Hatchard, *Proc. Chem. Soc., London*, 1962, 386-387.
4. C. A. Parker, in *Adv. Photochem.*, John Wiley & Sons, Inc., 1964, pp. 305-383.
5. T. N. Singh-Rachford and F. N. Castellano, *Coord. Chem. Rev.*, 2010, **254**, 2560-2573.

6. S. Baluschev, V. Yakutkin, T. Miteva, G. Wegner, T. Roberts, G. Nelles, A. Yasuda, S. Chernov, S. Aleshchenkov and A. Cheprakov, *New J. Phys.*, 2008, **10**, 013007.
7. R. R. Islangulov, J. Lott, C. Weder and F. N. Castellano, *J. Am. Chem. Soc.*, 2007, **129**, 12652-12653.
8. C. Weder, T. N. Singh-Rachford, J. Lott and F. N. Castellano, *J. Am. Chem. Soc.*, 2009, **131**, 12007-12014.
9. Y. C. Simon, S. Bai, M. K. Sing, H. Dietsch, M. Achermann and C. Weder, *Macromol. Rapid Commun.*, 2012, **33**, 498-502.
10. Y. C. Simon and C. Weder, *Chimia*, 2012, **66**, 878-878.
11. P. B. Merkel and J. P. Dinnocenzo, *J. Lumin.*, 2009, **129**, 303-306.
12. A. Monguzzi, R. Tubino and F. Meinardi, *J. Phys. Chem. A*, 2009, **113**, 1171-1174.
13. S. H. Lee, J. R. Lott, Y. C. Simon and C. Weder, *J. Mater. Chem. C*, 2013, **1**, 5142-5148.
14. A. Monguzzi, R. Tubino and F. Meinardi, *Int. J. Photoenergy*, 2008, 684196.
15. A. Monguzzi, R. Tubino and F. Meinardi, *Phys. Rev. B*, 2008, **77**, 155122.
16. Q. Li, C. Zhang, J. Y. Zheng, Y. S. Zhao and J. Yao, *Chem. Commun.*, 2012, **48**, 85-87.
17. Y. S. Zhao, C. Zhang, J. Y. Zheng and J. N. Yao, *Chem. Commun.*, 2010, **46**, 4959-4961.
18. A. Monguzzi, M. Frigoli, C. Larpent, R. Tubino and F. Meinardi, *Adv. Funct. Mater.*, 2012, **22**, 139-143.
19. Y. C. Simon, S. Bai, M. K. Sing, H. Dietsch, M. Achermann and C. Weder, *Macromol. Rapid Commun.*, 2012, **33**, 498-502.
20. J.-H. Kang and E. Reichmanis, *Angew. Chem. Int. Ed.*, 2012, **51**, 11841-11844.
21. J.-H. Kim and J.-H. Kim, *J. Am. Chem. Soc.*, 2012, **134**, 17478-17481.
22. C. Wohnhaas, A. Turshatov, V. Mailänder, S. Lorenz, S. Baluschev, T. Miteva and K. Landfester, *Macromol. Biosci.*, 2011, **11**, 772-778.
23. J. S. Lissau, J. M. Gardner and A. Morandeira, *J. Phys. Chem. C*, 2011, **115**, 23226-23232.
24. V. Jankus, E. W. Snedden, D. W. Bright, V. L. Whittle, J. A. G. Williams and A. Monkman, *Adv. Funct. Mater.*, 2013, **23**, 384-393.
25. P. E. Keivanidis, S. Baluschev, T. Miteva, G. Nelles, U. Scherf, A. Yasuda and G. Wegner, *Adv. Mater.*, 2003, **15**, 2095-+.
26. A. Monguzzi, R. Tubino, S. Hoseinkhani, M. Campione and F. Meinardi, *PCCP*, 2012, **14**, 4322-4332.
27. J. H. ter Horst, M. A. Deij and P. W. Cains, *Cryst. Growth Des.*, 2009, **9**, 1531-1537.
28. B. T. Makowski, B. Valle, K. D. Singer and C. Weder, *J. Mater. Chem.*, 2012, **22**, 2848-2850.
29. J. A. Hinke, T. J. Pundsack, W. A. Luhman, R. J. Holmes and D. A. Blank, *J.Chem. Phys.*, 2013, **139**, 101102.
30. T. Dienel, H. Proehl, T. Fritz and K. Leo, *J. Lumin.*, 2004, **110**, 253-257.
31. V. N. Knyukshto, A. M. Shul'ga, E. I. Sagun and É. I. Zen'kevich, *Opt. Spectrosc.*, 2006, **100**, 590-601.
32. J. Mezyk, R. Tubino, A. Monguzzi, A. Mech and F. Meinardi, *Phys. Rev. Lett.*, 2009, **102**, 087404.

Journal Name

RSCPublishing

COMMUNICATION

TOC Text and Figure

Green-to-blue upconverting molecular glasses consisting of a metal octaethylporphyrin sensitizer and a diphenyl anthracene derivative as emitting matrix are reported.