PERSPECTIVE

Molecular-based upconversion in homo/heterogeneous liquids and in micro/nanostructured solid materials

L. Latterini,[a] G. Massaro,[a,d] M.Penconi,[a,e] P. L. Gentili,[a] C. Roscini[c] and F. Ortica*[ab]

Radiation upconversion can be an elegant and efficient strategy to minimize wastes in energy harvesting and storage processes. The upconversion based on triplet-triplet annihilation processes of molecular dyes is a very versatile approach, but it requires a systematic photophysical characterization of the systems to optimize the upconversion yields and develop materials for technological applications. This paper represents an overview of the work carried out in our laboratories for the study and characterization of a molecular dye pair, 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrin platinum(II) (PtOEP) and 1,3,6,8-tetraphenylpyrene (TPPy), suitable as sensitizer and emitter, respectively, in a triplet-triplet annihilation based upconversion process. The investigation has been carried out in various media, such as homogeneous solvents of different viscosities, oil-in-water microemulsions, to end up with environments much closer to those required for potential applications, like nanostructured silica matrices and liquid filled micro/nanocapsules that provide upconversion to solid materials. The possibility to achieve upconversion emission even in confined and rigid media has been confirmed and can inspire further applications of the process.

Introduction

Triplet-triplet annihilation upconversion (TTA-UC) based on coordination compounds and organic molecules has been receiving notable attention since the last fifteen years, even though the phenomenon dates back to the sixties.[1,2] TTA-UC is usually accomplished by means of coordination compounds such as a metallated porphyrin, which behaves as antenna in the visible region and can sensitize an organic molecule characterized by high quantum yield of fluorescence, like a polycyclic aromatic hydrocarbon, which plays the role of a higher-energy emitter. The possibility to obtain TTA-UC upon low-energy, non-coherent excitation has triggered the interest of many researchers working on various fields;[3-61] the potential application to bioimaging and the integration with solar cells are no doubt intriguing.[62-65] However, the realization of practical devices usually requires the incorporation of the sensitizer and the emitter in a rigid medium or a solid matrix[37,41,46,47,57,66-71] where generally a significant decrease of the

upconversion emission quantum yield and intensity has been reported.[67,72-73]

Our first approach to TTA-UC was motivated by the attempt to minimize the waste of solar visible photons in the study of solid solutions of metal oxides as heterogeneous photocatalysts for hydrogen production from water.[74-78]

Herein, we report an overview of our research activity in this field, where the 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrin platinum(II) (PtOEP) and the 1,3,6,8-tetraphenylpyrene (TPPy) were investigated in their roles of sensitizer and emitter, respectively, in a TTA based upconversion process. We report our previous studies carried out in homogeneous solutions[79-80], oil-in-water microemulsions,[80] silica nanoparticles[81] and the preliminary results of unpublished works in liquid-filled microcapsules. Though most of the work was carried out using the PtOEP/TPPy as UC pair, some interesting results were also obtained by using 9,10-diphenyl anthracene (DPA) as emitter. The latest developments and future perspectives are also presented.

Results and discussion

Study in homogeneous solutions: UC pair optimization

The first step was the choice of a suitable pair of compounds which could work as sensitizer and emitter, respectively. As far as the antenna component is concerned, our attention was drawn by porphyrin molecules, which usually exhibit two absorption features: the Soret band, in the near UV region, and the Q band, located above 500 nm. The latter band is particularly interesting since it can be excited by low-frequency visible radiation. We took two porphyrin molecules into consideration, namely PdOEP and PtOEP.[79] As for the emitter species, TPPy, a polycyclic aromatic

a. Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia, Via Elce di Sotto 8, 06123 Perugia, Italy. Email: fausto.ortica@unipg.it
b. Istituto Nazionale di Fisica Nucleare (INFN), Sezione di Perugia, Via Pascoli, 06123 Perugia, Italy
c. Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and The Barcelona Institute of Science and Technology, Campus UAB, Bellaterra, 08193 Barcelona, Spain
d. Present Address: Institute of Chemical Research of Catalonia (ICIQ), Avda. Països Catalans, 16, 43007 Tarragona, Spain
e. Present Address: ISTM-CNR, via Golgi 19, 20133 Milano, Italy
† Footnotes relating to the title and/or authors should appear here.
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

hydrocarbon having an almost unitary quantum yield of fluorescence (ϕ_F = 0.96 ± 0.05)[82] was chosen. The lowest triplet excited state of TPPy only lies a few cm^{-1} above the triplet states of the porphyrin sensitizers and we have shown[79] that the collisional Dexter energy transfer between the triplet states of the antenna and the emitter can anyway occur driven by the contribution of the entropy of mixing to the Gibbs free energy, as previously reported in the literature.[83] This energy difference is 221 cm^{-1} and 665cm^{-1} in the case of the two couples PtOEP/TPPy and PdOEP/TPPY, respectively. We investigated the energy transfer process between the sensitizer and the emitter in deoxygenated media to increase the sensitizer decay time and increase the energy transfer probability, obtaining the Stern-Volmer constant and the quenching kinetic parameters (K_{SV} = 47600 ± 900 dm^3mol^{-1}, k_Q = (5.3 ± 0.1) ×10^8 dm^3mol^{-1} s^{-1} and K_{SV} = 15400± 900 dm^3mol^{-1}, k_Q = (3.35 ± 0.07) ×10^7 dm^3mol^{-1} $s^{-1}$for PtOEP and PdOEP, respectively).[79] Based on these data the PtOEP-TPPy pair allows for the most efficient energy transfer. Moreover, the presence of the Pt heavy atom enhances the spin-orbit coupling in the system, thereby increasing the kinetic constant for the collisional Dexter energy transfer between the triplet states of the antenna and the emitter. Thus, we selected the PtOEP-TPPy pair (Figure 1) to continue our investigation.

Figure 1

Fig. 1 Molecular structures of PtOEP and TPPy.

In our experiments, excitation was carried out by the non-coherent emission of a Xe lamp at 536 nm, at a low incident power of a few hundred Wm^{-2}, comparable to the solar irradiance in AM 1.5 conditions integrated across the Q-band of the porphyrin sensitizers (for experimental details, see refs. 79-81). Under these conditions, the k_Q can be identified with the kinetic constant which characterizes the energy transfer process:

$$T_1(sensitizer) + S_0(emitter) \rightarrow S_0(sensitizer) + T_1(emitter)$$
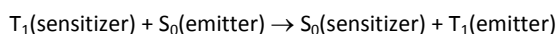
The choice of the PtOEP/TPPy as the sensitizer/emitter pair in the UC experiment also allows a high portion of the emitted light from the TPPy to be collected without any significant re-absorption by the porphyrin sensitizer, whose Q band is red-shifted with respect to TPPy fluorescence, as it can be seen in Figure 2.

Figure 2

Fig. 2 Normalized absorption (full line) and emission (dashed line) spectra of PtOEP (red) and TPPy (blue) in toluene.

Toluene was chosen as a suitable solvent to solubilise the two compounds and perform the upconversion experiments. The following step was then the optimization of the concentration ratio of the two compounds PtOEP and TPPy. Therefore, we explored the dependence of the upconversion quantum yield, ϕ_{UC}, on the concentrations of the sensitizer and the emitter involved in the process. The porphyrin content was fixed at the order of magnitude of 1×10^{-5} mol dm^{-3}, while the concentration of the emitter was varied in the range from 6×10^{-5} mol dm^{-3} to 3×10^{-3} mol dm^{-3}.The

maximum value of green-to-violet upconverted emission, ϕ_{UC} = 3.8%, was found for a concentration ratio of 60 between [TPPy] and [PtOEP], under irradiation with an intensity of 133 W m^{-2}.[79]

Study in homogeneous solutions: solvent effects

Later on, we investigated the role of the medium; bromobenzene and anisole were used as solvents, instead of toluene. Even though they have similar structure, their viscosities increase from toluene to anisole, passing through bromobenzene; furthermore, the latter has a heavy atom (Br) in its structure, which could influence the spin-orbit coupling in the system. The measurements were carried out under the same experimental conditions, using an excitation intensity of 194 Wm^{-2} at 536 nm. For all the three solvents, the highest upconversion quantum yields (Table 1) were obtained at a concentration ratio of 60 between the emitter and the sensitizer, that is [PtOEP] = 1×10^{-5} mol dm^{-3} and [TPPy] = 6×10^{-4} mol dm^{-3}, as already found in our previous experiments. The ϕ_{UC} value is by far highest in toluene, where the lowest viscosity makes the molecular diffusion easier and therefore enhances the efficiency of both the triplet-triplet energy transfer process from the PtOEP to the TPPy and the TTA. Furthermore, in the same solvent, PtOEP exhibits the lowest ϕ_P and k_P values, thereby indicating that the radiative deactivation of the donor triplet state, which competes with the energy transfer process to the TPPy molecule, gives a minor contribution in toluene than in the other two solvents explored.

Tab. 1 Lifetimes (τ_P), quantum yields (Φ_P) and rate constants (k_P) of phosphorescence of PtOEP and upconversion quantum yields (Φ_{UC}) for the pair PtOEP and TPPy in the three solvents having different viscosity (η).

Table 1

PtOEP and TPPy in oil-in-water microemulsions

The possibility to solubilise the upconverting couple PtOEP-TPPy in a confined environment, thus favouring the encounter of the two species and possibly enhancing the quantum yield of the process, induced us to investigate the effect of the inclusion of the sensitizer and the emitter molecules in an oil-in-water microemulsion. Based on the aforementioned results and the high ϕ_{UC} measured in toluene, we prepared a toluene-based micro-heterogeneous system with TX-100 and 1-pentanol as surfactant and co-surfactant agents, respectively, that allow for the stabilization of oil droplets in which the sensitizer-emitter couple are solubilized. This mixture allowed us to obtain an optically transparent oil-in-water microemulsion.[80] However, due to solubility issues of the solutes in the toluene pools, it was impossible to load the microemulsions with sensitizer and emitter contents higher than a ratio [TPPy]/[PtOEP] equal to 10. This fact, along with an increase of the ϕ_P for PtOEP (from 0.41 in pure toluene to 0.71 in the microemulsion) and a decrease of the ϕ_F for TPPy (from 1 in toluene to 0.62 in the microemulsion), both detrimental to the up-conversion process, brought about a significant decrease of ϕ_{UC} in the oil-in water microemulsion compared to the toluene solution. Indeed, upon irradiation at 536 nm with an excitation intensity of 194 W m^{-2}, the ϕ_{UC} dropped from 0.19 in pure toluene down to 0.01 in the heterogeneous system, confirming what had previously been reported in similar upconversion experiments in surfactant aqueous solution[84] and in a water environment.[85] One of the possible ways to overcome this

obstacle might be increasing the toluene cavity inside the oil-in-water microemulsion, but this would require a modification of the microemulsion composition and structure.

Measurements in silica matrices

Our further step, also taking into account some possible technological uses of the upconversion process, including integration with solar cells and biomedical applications, was the incorporation of the sensitizer and the emitter in solid matrices. The drawbacks of this strategy are well known[67,72], the most important being the strong decrease of the upconversion emission intensity under these experimental conditions. However, recent studies have reported the possibility of achieving intense emission signal even in these rigid media, once the dyes are pre-organized[86] or adequately arranged into the solid matrix.[87] Therefore, we prepared silica matrices loaded with the usual PtOEP/TPPy upconversion pair and having different morphologies, from a mesoporous microstructured silicate material (SBA) down to core-shell silica nanoparticles (NPs).[81]

In the first case, due to the sufficiently large pores of the matrix (4-14 nm)[88] high amounts of sensitizer and emitter could be loaded into the structure, with the possibility of keeping the ratio [TPPy]/[PtOEP] = 60 and enhancing the frequency of encounter between the species. Unfortunately, due to the formation of aggregates and excimer-like species, with consequent modification of the energy of the excited electronic states, and to the reduced mobility of the organic molecules arranged in crystals, no upconverted emission could be detected upon excitation of the SBA samples at 535 nm with an intensity of 190 W m^{-2}.

On the contrary, encapsulation of PtOEP and TPPy into silica nanoparticles (having a mean diameter of 10 nm[89,90] and a core-shell morphology), allowed the solubilization of the species, mainly in their monomeric forms, in the spherical core of the nanoparticles constituted by the hydrophobic part of the surfactant used as template to grow the silica shell. Under these conditions, the sensitizer and the emitter take advantage of the amorphous structure and less rigid environment of the core, thus enabling the dynamics required by the triplet-triplet annihilation upconversion. After deoxygenation of the NPs-loaded powder sample, both phosphorescence of the sensitizer (λ_{em} = 645 nm) and upconversion emission (λ_{em} = 430 nm) bands could indeed be detected (Figure 3).

Figure 3

Fig. 3 PtOEP phosphorescence (red) and upconversion emission (blue) spectra of NPs loaded with PtOEP and TPPy under nitrogen atmosphere. Inset: TEM image of the NPs.

Liquid-filled microcapsules

The soft core given by the hydrophobic moiety of the surfactant used in the silica nanoparticles provided the environment for the UC to occur. An alternative strategy that also allows increasing the soft portion of the particle consists in the preparation of liquid-filled capsules.[91] With mononuclear core-shell micro/nanocapsules, payloads as high as 90% can be obtained, which also guarantees a high UC dyes loading. These capsules are made by a liquid core and a solid polymeric shell, which confines and protects the internal part. The liquid core *a)* dissolves the antenna and emitting units and *b)* allows the dynamic bimolecular processes involved in the TTA-UC. The liquid-filled capsules can be used to achieve liquid-like behaviours even in their powder state.[92,93]

As proof-of-concept, polyurea (PU) microcapsules were prepared through the interfacial polymerization.[94] Polyurea is a crosslinked polymer, prepared from a polyisocyanate (i.e. Desmodour®N100) and diethylentriamine, which guarantees high internal liquid retention. As oil-core, Miglyol®812 (a capylic/capric triglyceride oil) was used for dissolving well the UC dyes and for its low volatility, which ensure a better capsules stability over time.[92] TPPy and PtOEP were used as UC dyes with a [TPPy]/[PtOEP] ratio of 60. For the capsules preparation, the organic phase (made of the oil, the dyes and the isocyanate) was emulsified (through magnetic stirring) into the water phase, containing a surfactant (polyvinyl alcohol) and the polyamine. After emulsifying for 5 min, upon heating the emulsion at 60 °C, spherical microcapsules of 70-200 μm were obtained. The suspension was freeze-dried over 2 days to achieve the final capsules powder.[95] The excitation of the de-oxygenated microcapsules powder with a pulsed and coherent 532 nm light of 300 Wm^{-2} resulted in the observation of both phosphorescence (of PtOEP, λ_{em} = 645 nm) and UC (of TPPy, λ_{em} = 430 nm) emissions (Figure 4). Unfortunately, the micrometric dimensions of the capsules give rise to some scattering of the excitation light. This fact prevented us, at this stage from determining the quantum yield for the upconversion process under our experimental conditions.

Figure 4

Fig. 4 a) Emission spectra of PUmicrocapsules loaded with PtOEP-TPPy (λ_{ex} = 532 nm) in Miglyol®812 Inset: digital photo of the freeze-dried capsules; b) SEM image of capsules.

Notably, these preliminary results showed that the capsules strategy allowed to observe UC in a solid system (capsules powder of Figure 4a), where generally this process is prevented by the lack of molecular diffusion.

The micro/nanoencapsulation is a quite versatile and general strategy since it allows to easily tune the oil core, the shell material and the dye pair, as well as the capsules size. Thus, the composition of the capsules can be modified maintaining the UC emission. For example, UC emission has been detected in PU microcapsules using hexadecane as oil and DPA as emitter instead of TPPy ([DPA]/[PtOEP]=30), (Figure 5).

Figure 5

Fig. 5 a) Emission spectra of PU microcapsules loaded with PtOEP-DPA (λ_{exc} = 532 nm) in hexadecane; b) SEM image of capsules.

The composition and dimensions of the capsules, together with their further photophysical characterization, are object of the ongoing research finalized to the optimization of these systems.

Conclusions

In this brief account, the investigation of a couple of molecular systems acting as sensitizer (PtOEP) and emitter (TPPy) in a triplet-triplet annihilation based upconversion process has been reported. Our studies have been carried out in various media, such as homogeneous solvents of different viscosities, oil-in-water microemulsions, nanostructured silica matrices and liquid filled micro/nanocapsules. The upconverting molecular systems have great potential developments due to large variety of organic and organo-metallic dyes whose electronic properties can be tuned to the expected behaviour through chemical functionalization or by controlling their molecular arrangements.

The proof-of-concept that UC properties are preserved also in solid phase in inorganic or organic media, as we have shown in the cases of nanostructured silica matrices and liquid filled microcapsules, opens the possibility to apply these systems in real devices.

Of course, important improvements are still necessary before the knowledge is transferred to devices production. Further measurements are object of the ongoing research in our laboratories, finalized to the optimization of these systems. The main aspects which have to be improved are the intensity of UC emission in solid phase and the scale-up of the synthetic procedures to obtain micro/nanocapsules, which would allow us to give a better quantitative definition of the upconversion quantum yields in these media.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Notes and references

1 C. A. Parker and C. G. Hatchard, *Proc. R. Soc. Lond. A*, 1962, **269**, 574-584.
2 C. A. Parker and C. G. Hatchard, *Proc. Chem. Soc., London*, 1962, 386-387.
3 A. L. Stevens, N. K. Joshi, M. F. Paige. and R. P. Steer, *J. Phys. Chem. B,* 2017*,* **121**, 11180-11188.
4 A. Monguzzi, A. Oertel, D. Braga, A. Riedinger, D. K. Kim, P. N. Knüsel, A. Bianchi, M. Mauri, R. Simonutti, D. J. Norris and F. Meinardi, *ACS Appl. Mater. Interfaces*, 2017, **9**, 40180-40186.
5 Y. Bai, J.-H. Olivier, H. Yoo, N. F. Polizzi, J. Park, J. Rawson and M. J. Therien, *J. Am. Chem. Soc.*, 2017, **139**, 16946-16958.
6 K. A. El Roza and F. N. Castellano, *Chem. Commun.*, 2017, **53**, 11705-11708.
7 K. Xu, J. Zhao and E. G. Moore, *J. Phys. Chem. C,* 2017, **121**, 22665-22679.
8 S. Chandrasekaran, Y.-L. Thi Ngo, L. Sui, E. J. Kim, D. K. Dang, J. S. Chung and S. H. Hur, *Dalton Trans.*, 2017, **46**, 13912-13919.
9 R Vadrucci, A. Monguzzi, F. Saenz, B. D. Wilts, Y. C. Simon and C. Weder, *Adv Mater.*, 2017, 1702992_1-1702992_8.
10 R. Rautela, N. K. Joshi, S. Novakovic, W. W. H. Wong, J.M. White, K. P. Ghiggino, M. F. Paige and R. P. Steer, *Phys. Chem. Chem. Phys.*, 2017, **19**, 23471-23482.
11 D. Dzebo, K. Moth-Poulsen and B. Albinsson, *Photochem. Photobiol. Sci.*, 2017, **16**, 1327-1334.
12 V. Gray, A. Dreos, P. Erhart, B. Albinsson, K. Moth-Poulsen and M. Abrahamsson, *Phys. Chem. Chem. Phys.*, 2017, **19**, 10931-10939.
13 S. H. C. Askes, V. C. Leeuwenburgh, W. Pomp, H. Arjmandi-Tash, S. Tanase, T. Schmidt and S. Bonnet, *ACS Biomater. Sci. Eng.*, 2017, **3**, 322–334.
14 H. Goudarzi and P. E. Keivanidis, *ACS Appl. Mater. Interfaces*, 2017, **9**, 845-857.
15 B. Tian, Q. Wang, Q. Su, W. Feng and F. Li, *Biomaterials*, 2017, **112**, 10-19.
16 S. Baluschev, K. Katta, Y. Avlasevich and K. Landfester, *Mater. Horiz.*, 2016, **3**, 478-486.
17 K. Okumura, K. Mase, N. Yanai and N. Kimizuka, *Chem. Eur. J.* 2016, **22**, 1-7.
18 C. Ye, L. Zhou, X. Wang and Z. Liang, *Phys. Chem. Chem. Phys.*, 2016, **18**, 10818-10835.
19 C. E. McCusker, F. N. Castellano, *Top Curr. Chem. (Z)*, 2016, **374**, 1-25.
20 F. Deng, A. J. Francis, W. W. Weare and F. N. Castellano, *Photochem. Photobiol. Sci.*, 2015, **14**, 1265-1270.
21 K. Katta, D. Busko, Y. Avlasevich, R. Muñoz-Espí, S. Baluschev and K. Landfester, *Macromol. Rapid Commun.*, 2015, **36**, 1084-1088.
22 S. Hoseinkhani, R. Tubino, F. Meinardi and A. Monguzzi, *Phys. Chem. Chem. Phys.*, 2015, **17**, 4020-4024.
23 A. Nattestad, Y. Y. Cheng, R. W. Mac Queen, T. F. Schulze, F. W. Thompson, A. J. Mozer, B. Fückel, T. Khoury, M. J. Crossley, K. Lips, G. G. Wallace and T. W. Schmidt, *J. Phys. Chem. Lett.*, 2013, **4**, 2073-2078.
24 F. Deng, J. R. Sommer, M. Myahkostupov, K. S. Schanze and F. N. Castellano, *Chem. Commun.*, 2013, **49**, 7406-7408.
25 F. Deng, W. Sun and F. N. Castellano, *Photochem.Photobiol. Sci.*, 2014, **13**, 813-819.
26 V. Yakutkin, S. Aleshchenkov, S. Chernov, T. Miteva, G. Nelles, A. Cheprakov and S. Baluschev, *Chem. Eur. J.*, 2008, **14**, 9846–9850.
27 J.-H. Olivier, Y. Bai, H. Uh, H. Yoo, M.J. Therien and F.N. Castellano, *J.Phys.Chem. A*, 2015, **119**, 5642-5649.
28 A. Monguzzi and F. Meinardi, *J. Phys. Chem. A*, 2014, **118**, 1439–1442.
29 K. Börjesson, D. Dzebo, B. Albinsson and K. Moth-Poulsen, *J. Mater. Chem. A*, 2013, **1**, 8521-8524.
30 X. Cao, B. Hu and P. Zhang, *J. Phys. Chem. Lett.*, 2013, **4**, 2334-2338.
31 S. H. Lee, J. R. Lott, Y. C. Simon and C. Weder, *J. Mater. Chem. C*, 2013, **1**, 5142-5148.
32 C. Zhang, J. Zhao, S. Wu, Z. Wang, W. Wu, J. Ma, S. Guo and L. Huang, *J. Am. Chem. Soc.*, 2013, **135**, 10566-10578.
33 S. K. Sugunan, C. Greenwald, M. F. Paige and R. P. Steer, *J. Phys. Chem. A*, 2013, **117**,5419-5427.
34 W. Wu, J. Sun, X. Cui and J. Zhao, *J. Mater. Chem. C*, 2013, **1**, 4577-4589.
35 C. Wohnhaas, K.Friedemann, D. Busko, K. Landfester, S. Baluschev, D. Crespy and A. Turshatov, *ACS Macro Lett.*, 2013, **2**, 446-450.
36 F. Deng, J. Blumhoff and F. N. Castellano, *J. Phys. Chem. A*, 2013, **117**, 4412-4419.

ARTICLE

37 A. Monguzzi, F. Bianchi, A. Bianchi, M. Mauri, R. Simonutti, R. Ruffo, R. Tubino and F. Meinardi, *Adv. Energy Mater.*, 2013, **3**, 680-686.

38 J. Zhao, S. Ji and H. Guo, *RSC Adv.*, 2011, **1**, 937-950.

39 Y. Y. Cheng, B. Fückel, T. Khoury, R. G. C. R. Clady, N. J. Ekins-Daukes, M. J. Crossley and T. W. Schmidt*, J. Phys. Chem. A*, 2011, **115**, 1047-1053.

40 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_1-013007_12.

41 T. Miteva, V. Yakutkin, G. Nelles and S. Baluschev, *New J. Phys.*, 2008, **10**, 103002_1-103002_10.

42 S. Baluschev, T. Miteva, V. Yakutkin, G. Nelles, A. Yasuda and G. Wegner, *Phys. Rev. Lett.*, 2006, **97**, 143903_1-143903_3.

43 S. Baluschev, V. Yakutkin, T. Miteva, Y. Avlasevich, S. Chernov, S. Aleshchenkov, G. Nelles, A. Cheprakov, A. Yasuda, K. Müllen, and G. Wegner, *Angew. Chem. Int. Ed.*, 2007, **46**, 7693-7696.

44 S. Baluschev, V. Yakutkin, G. Wegner, B. Minch, T. Miteva, G. Nelles and A. Yasuda, *J. Appl. Phys.*, 2007, **101**, 023101_1-023101_5.

45 S. Baluschev, V. Yakutkin, G. Wegner, T. Miteva, G. Nelles, A. Yasuda, S. Chernov, S. Aleshchenkov and A. Cheprakov, *J. Appl. Phys.*, 2007, **90**, 181103_1-181103_4.

46 T.N. Singh-Rachford, F. N. Castellano, *Coordin. Chem. Rev.*, 2010, **254**, 2560-2573.

47 R. R. Islangulov, J. Lott, C. Weder and F. N. Castellano, *J. Am. Chem. Soc.*, 2007, **129**, 12652-12653.

48 R. R. Islangulov, D. V. Kozlov and F. N. Castellano, *Chem. Commun.*, 2005, 3776-3778.

49 T. N. Singh-Rachford and F. N. Castellano, *J. Phys. Chem. A*, 2009, **113**, 5912-5917.

50 T. N. Singh-Rachford and F. N. Castellano, *Inorg. Chem.*, 2009, **48**, 2541-2548.

51 T. N. Singh-Rachford, A. Nayak, M. L. Muro-Small, S. Goeb, M. J. Therien and F. N. Castellano, *J. Am. Chem. Soc.*, 2010, **132**, 14203-14211.

52 A. Monguzzi, R. Tubino, S. Hoseinkhani, M. Campione and F. Meinardi, *Phys. Chem. Chem. Phys.*, 2012, **14**, 4322-4332.

53 A. Monguzzi, M. Frigoli, C. Larpent, R. Tubino and F. Meinardi, *Adv. Funct. Mater.*, 2012, **14**, 139-143.

54 A. Monguzzi, R. Tubino and F. Meinardi, *Nuovo Cimento B*, 2010, **125**, 569-578.

55 A. Monguzzi, R. Tubino and F. Meinardi, *Phys. Rev. B*, 2008, **77**, 155122_1-155122_4.

56 A. Monguzzi, J. Mezyk, F. Scotognella, R. Tubino, and F. Meinardi, *Phys. Rev. B*, 2008, **78**, 195112_1-195112_5.

57 A. Monguzzi, R.Tubino and F. Meinardi, *J. Phys. Chem. A*, 2009, **113**, 1171-1174.

58 S. K. Sugunan, U. Tripathy, S. M. K. Brunet, M. F. Paige and R. P. Steer, *J. Phys. Chem. A*, 2009, **113**, 8548-8556.

59 P. Ceroni, *Chem. Eur. J.*, 2011, **17**, 9560-9564.

60 D. Wei, F. Ni, Z. Zhu, Y. Zoub and C. Yang, *J. Mater. Chem. C*, 2017, **5**, 12674-12677.

61 Y. Murakami, S. Kumar Das, Y. Himuro and S. Maeda, *Phys.Chem.Chem.Phys.*, 2017, **19**, 30603-30615.

62 Z. Jiang, M. Xu, F. Li and Y. Yu, *J. Am. Chem. Soc.*, 2013, **135**, 16446-16453.

63 R. S. Khnayzer, J. Blumhoff, J. A. Harrington, A. Haefele, F. Deng and F. N. Castellano, *Chem. Comm.*, 2012, **48**, 209-211.

64 V. Gray, D. Dzebo, M. Abrahamsson, B. Albinsson and K. Moth-Poulsen, *Phys. Chem. Chem. Phys.*, 2014, **16**, 10345-10352.

65 S. H. C. Askes, A. Bahreman and S. Bonnet, *Angew. Chem. Int. Ed.*, 2014, **53**, 1029-1033.

66 J. de Wild, A. Meijerink, J. K. Rath, W. G. J. H. M. Van Sark and R. E. I. Schropp, *Energy Environ. Sci.*, 2011, **4**, 4835-4848.

67 T. N. Singh-Rachford, J. Lott, C. Weder, and F. N. Castellano, *J. Am. Chem. Soc.*, 2009, **131**, 12007-12014.

68 P. E. Keivanidis, S. Baluschev, G. Lieser and G. Wegner, *ChemPhysChem*, 2009, **10**, 2316-2326.

69 P. B. Merkel and J. P. Dinnocenzo, *J. Lumin.*, 2009, **129**, 303-306.

70 S. Baluschev, F. Yu, T. Miteva, S. Ahl, A. Yasuda, G. Nelles, W. Knoll and G. Wegner, *Nano Lett.*, 2005, **5**, 2482-2484.

71 J. A. O'Brien, S. Rallabandi, U. Tripathy, M. F. Paige and R. P. Steer, *Chem. Phys. Lett.*, 2009, **475**, 220-222.

72 Y.C. Simon and C. Weder, *J. Mater. Chem.*, 2012, **22**, 20817-20830.

73 J. Mezyk, R. Tubino, A. Monguzzi, A. Mech, and F. Meinardi, *Phys. Rev. Lett.*, 2009, **102**, 087404_1-087404_4

74 **P.** L. Gentili, M. Penconi, F. Costantino, P. Sassi, F. Ortica, F. Rossi and F. Elisei, *Sol. Energy Mater. Sol. Cells*, 2010, **94**, 2265-2274.

75 P. L. Gentili, M. Penconi, F. Ortica, F. Cotana, F. Rossi and F. Elisei, *Int. J. Hydrogen Energy*, 2009, **34**, 9042-9049.

76 P. L. Gentili, F. Rossi, M. Penconi, F. Ortica and F. Elisei, Expert Commentary in D. Honnery, P. Moriarty (Eds.) Hydrogen Production, Nova Science Publishers, Inc., 2012, Ch. 14, 411-420.

77 M.Penconi, F.Rossi, F.Ortica, F.Elisei and P.L.Gentili, *Sustainability*, 2015, **7**, 9310-9325.

78 M.Penconi, A.Cesaretti, F.Ortica, F.Elisei and P.L.Gentili, *J. Lumin.*, 2016, **177**, 314-324.

79 M. Penconi, F. Ortica, F. Elisei and P. L. Gentili*, J. Lumin.*, 2013, **135**, 265-270.

80 M. Penconi, P. L. Gentili, G. Massaro, F. Elisei and F. Ortica, *Photochem.Photobiol. Sci.*, 2014, **13**, 48-61.

81 G. Massaro, P. L. Gentili, V. Ambrogi, M. Nocchetti, F. Marmottini, F. Ortica and L. Latterini, *Microporous Mesoporous Mater.*, 2017, **246**, 120-129.

82 L. C. Pereira, I. C. Ferreira and M. P. F. Thomaz, *J. Photochem.*, 1978, **9**, 363-367

83 Y. Yap Cheng, B. Fückel, T. Khoury, R. G. C. R. Clady, N. J. Ekins-Daukes, M. J. Crossley and T. W. Schmidt, *J. Phys. Chem. A*, 2011, **115**, 1047-1053.

84 Turshatov, D. Busko, S. Baluschev, T. Miteva and K. Landfester, *New J. Phys.*, 2011, **13**, 083035_1-083035_11.

85 K. Tanaka, K. Inafuku and Y. Chujo, *Chem. Commun.*, 2010, **46**, 4378-4380.

86 P. Mahato, N. Yanai, M. Sindoro, S. Granick and N. Kimizuka, *J. Am. Chem. Soc.*, 2016, **138**, 6541-6549.

87 G. Massaro, J. Hernando, D. Ruiz-Molina, C. Roscini and L. Latterini, *Chem. Mater.*, 2016, **28**, 738-745.

88 V. Ambrogi, F. Marmottini and C. Pagano, *Microporous Mesoporous Mater.*, 2013, **177**, 1-7.7

89 Q. Huo, J. Liu, L.-Q. Wang, Y. Jiang, T. N. Lambert and E. Fang, *J. Am. Chem. Soc.*, ,2006, **128**, 6447-6453.

90 Q. Liu, T. Yang, W. Feng and F. Li, *J. Am. Chem. Soc.*, 2012, **134**, 5390–5397.

91 S. Gouin, *Trends Food Sci. Technol.*, 2004, **15**, 330-347.

92 N. Vazquéz-Mera, C. Roscini, J. Hernando and D. Ruìz-Molina, *Adv. Functional Mater.*,2015, **25**, 4129-4134.

93 N. Vazquéz-Mera, C. Roscini, J. Hernando and D. Ruìz-Molina, *Adv. Optical Mater.*,2013, **1**, 631-636.

94 K. Hong and S. Park, *Mat. Sci. Eng. A*,1999, **272**, 418-421.

95 H. N. Yow and A. F. Routh, *Soft Matter*, 2006, **2**, 940–949.