FULL PAPER

Low-Power-Photon Up-Conversion in Dual-Dye-Loaded Polymer Nanoparticles

Angelo Monguzzi,* Michel Frigoli, Chantal Larpent, Riccardo Tubino, and Francesco Meinardi

Sensitized triplet–triplet annihilation in multicomponent organic systems is already demonstrated to be suitable for obtaining efficient up-conversion in solution with excitation power densities comparable to solar irradiance, but loses efficiency in the solid state. Here, it is demonstrated that it is possible to reduce this limitation by incorporating a standard bicomponent system in polymer nanoparticles. The confinement of all of the involved photophysical processes in a nanometer-scale volume makes each nanoparticle a single and isolated high-efficiency up-converting unit. As a consequence, these dual-dye-loaded nanoparticles can be used to produce drop-cast films, as well as dopants for polymeric matrices, preserving the performances of the starting moieties in solution.

1. Introduction

People working on renewable energy sources have been trying to up-convert the solar spectrum to recover the large number of low-energy photons that are not exploited by photovoltaic devices and in photocatalytic electrochemical cells for hydrogen production.[1–5] Indeed, this goal cannot be achieved by traditional approaches, as second-harmonic generation or two-photon absorption requires power densities several orders of magnitude larger than solar irradiance.[6] In the last few years, a new strategy to obtain up-conversion at low power and with non-coherent radiation has been pursued.[7–10] It is based on bicomponent organic systems operating through the following sequence of photophysical steps: i) absorption of light by a donor molecule, producing singlet excited states; ii) intersystem crossing (ISC) switching the excitation from singlet to triplet states; iii) energy transfer (ET) towards the metastable triplet states of an acceptor molecule; and iv) triplet-triplet annihilation (TTA) giving rise to high-energy singlet excited states of the acceptor moiety, leading to up-converted emission (see Figure S1E, Supporting

Information).[11–21] In such a way, efficient up-conversion has been demonstrated in liquid systems at excitation power densities as low as 0.1 mW cm^{-2}.[14] Despite these results, the fabrication of devices suitable for practical applications appears still far away, since it is quite difficult to obtain high-efficiency solid-state systems. Indeed, the largest up-conversion efficiency reported up to now for a rigid polymeric matrix is as low as 0.02%.[22] Moreover, a direct comparison between the performance of the same bicomponent system in solution versus the solid state shows that, in the latter, the up-conversion efficiency drops by a factor of 100–1000.[23] The origin of this difference is the large molecular mobility in solution, which strongly enhances the interaction probability and, as a consequence, enhances both the ET and TTA processes. On the contrary, in rigid, polymeric co-doped films, the lack of any relevant molecular mobility is only partially counterbalanced by the ability of the excited states to migrate, because of the rather-short exciton diffusion lengths. When considering crystalline systems, despite the fact that they are not very appealing for the realization of low-cost devices, the situation is not much better. Here, the typical exciton diffusion lengths may be comparable with those of small molecules in low-viscosity solvents, but the donor and acceptor moieties (usually metalloporphyrins and oligoacenes, respectively) tend to segregate into two independent frameworks.

In this communication, we report an original approach to incorporate bicomponent organic systems for high-efficiency sensitized up-conversion in the solid state. We embedded a proper combination of two donor-acceptor dyes within polymeric nanoparticles (NPs) that acted as a container. Since each NP behaves as a high-efficiency single and isolated up-converting unit, they can be dispersed in a liquid solvent, used as a dopant in polymeric matrices or employed to produce drop-cast films, preserving their intrinsic efficiency and allowing the tuning of the doped-material optical density. We want to underline that the proposed approach is not peculiar of a specific colorant or plastic host.[24–32] Indeed, the idea of including interacting species in nanometer-scale shells is, on the contrary, quite general and easily adaptable for a large number of small molecules exploited in sensitized up-conversion and other photonic applications. Moreover, as an additional but fundamental benefit, the NPs were prepared to completely shield the dyes from the external environment, and especially from oxygen,

Dr. A. Monguzzi, Prof. R. Tubino, Prof. F. Meinardi
Dipartimento di Scienza dei Materiali
Università Milano Bicocca
via R. Cozzi 53, 20125 Milano, Italy
E-mail: angelo.monguzzi@mater.unimib.it
Dr. M. Frigoli, Prof. C. Larpent
Institut Lavoisier UMR-CNRS 8180
Université de Versailles Versailles-Saint Quentin en Yvelines 45
Avenue des Etats-Unis, 78035 Versailles Cedex, France

FULL PAPER

which is a quencher of all of the metastable triplets involved in the up-conversion process.[33,34]

2. Results and Discussion

In order to demonstrate the validity of the proposed strategy, we selected two among the best and most-investigated dyes for sensitized up-conversion: Pt(II)octaethylprophyrin (PtOEP), which acts as the light harvester and donor, and 9,10-diphenylanthracene (DPA), which acts as the energy acceptor and final emitter (**Figure 1**a). These two dyes have been embedded within cross-linked polystyrene-based nanoparticles (NPs) of 16 nm diameter, obtained as a stable aqueous suspension by polymerization in an oil-water microemulsion stabilized with a cationic surfactant (dodecyltrimethylammonium bromide (DTAB)) (Figure 1b).[35,36] The embedding process within the NP core was obtained by swelling with a dichloromethane (DCM) solution of DPA and PtOEP (50:1 molar ratio), followed by evaporation of the solvent.[37–41] The average loading of each NP was one PtOEP molecule and 50 DPA molecules (see "NP Preparation and Doping" in the Experimental Section).
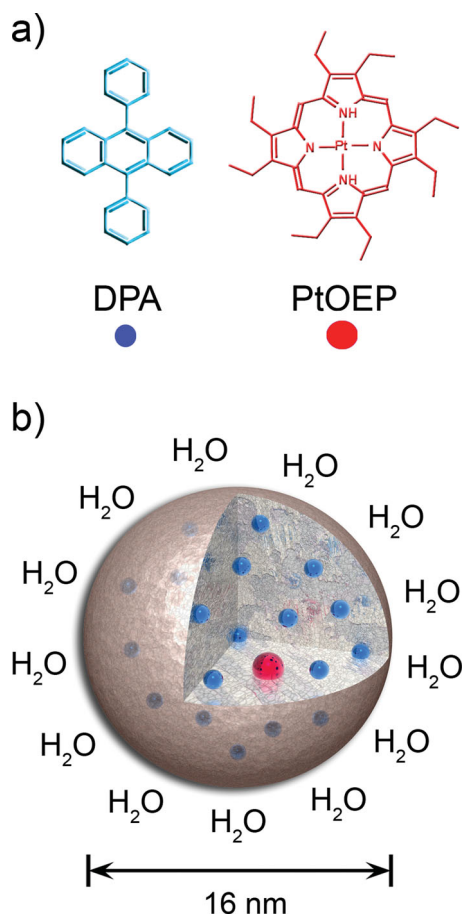

Figure 1. a) Molecular structure of the compounds in the study. b) Schematic representation of a dual-doped nanoparticle with PtOEP (red sphere) and DPA (blue spheres), showing the shielding from the external environment exerted by the NPs.
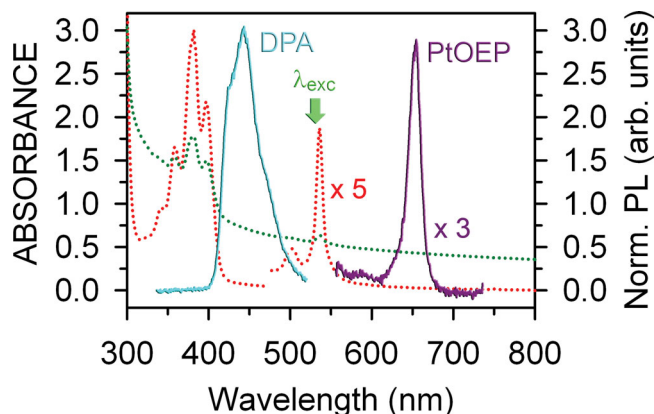

Figure 2. UV–vis absorption spectrum of NP_{Susp}, 25 μmol of NP L^{-1} (red dotted line) and NP_{Film} (green dotted line) with an optical path of 0.1 cm. The solid lines are the normalized photoluminescence (PL) spectra for the NP_{Susp} sample under excitation at 532 nm with a power density of 0.03 W cm^{-2}. Laser stray-light has been removed for clarity.

The up-conversion effect was studied, as described in the Experimental Section, by continuous-wave (CW) and time-resolved photoluminescence measurements on dye-loaded NPs in a colloidal aqueous suspension (NP_{Susp}, 25 μmol of NPs per litre) and drop-cast films (NP_{Film}).

Figure 2 shows the absorption spectra for NP_{Susp} and NP_{Film} (data regarding suspensions with different NP concentrations are shown in Figure S2E, S3E and S4E, Supporting Information). The absorption of the DPA and PtOEP in the NPs was very similar to that in solution. This indicates that the chromophores behave as monomeric species, suggesting that the distances between the chromophores were large enough to prevent the formation of dimeric species or π–π interactions between the neighbouring chromophoric groups, in agreement with a homogeneous dispersion of the dyes. The vibronic band centered on 375 nm is due to the DPA S_0-S_1 allowed transition, while the narrow peak at 536 nm is the Q-band of the porphyrin. The large background detectable in the absorption spectrum of NP_{Film} was produced by the light scattering of the NPs in the cast film. NPs of both samples, when excited at 532 nm in the PtOEP Q-band, gave rise to a bright, up-converted emission at CW excitation intensities of less than 10 mW cm^{-2}. The same behavior was preserved in the cast film.

Time-resolved photoluminescence (PL) measurements provided a description of the donor-acceptor ET process inside the NPs. The decay of the residual PtOEP phosphorescence at 645 nm was clearly biexponential (**Figure 3**) with characteristic lifetimes of $\tau_1 = 72.1$ μs and $\tau_2 = 8.9$ μs for NP_{Susp} and $\tau_1 = 63.7$ μs and $\tau_2 = 8.3$ μs for NP_{Film}. This biexponential decay suggests that the PtOEP molecules were in two different local environments within the NP. The slow PL component τ_1 of about 70 μs is comparable to the natural lifetime ($\tau_0 = 65.0$ μs) of the PtOEP phosphorescence measured in oxygen-free THF solution (see Figure S5E, Supporting Information). Therefore, a fraction of the PtOEP molecules does not seem to be able to transfer its excitation to the DPA, probably because of the statistical distribution of the dyes inside each NP. Consequently, the red emission of the PtOEP was still observed. Optimizing the
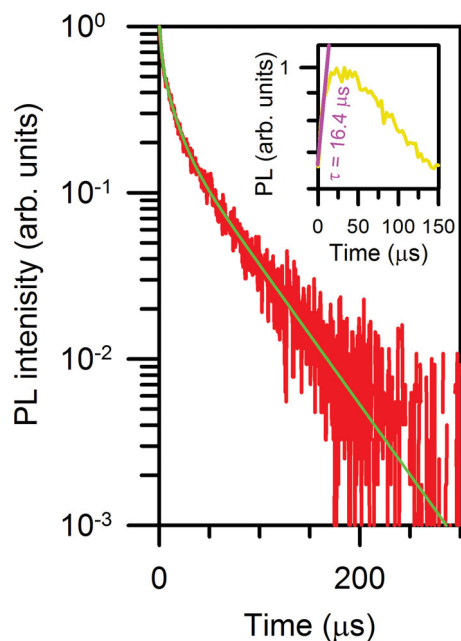
Figure 3. PL decay of the NP_{Susp} luminescence at 645 nm (PtOEP emission) under an average excitation power density of 3 mW cm^{-2} at 200 Hz. The decay follows a biexponential behavior, with characteristic lifetimes of $\tau_1 = 71.2$ μs and $\tau_2 = 8.9$ μs. The inset shows the DPA PL during the first 150 μs, where it is possible to appreciate the rise of the blue emission in NP_{Susp}.

concentration ratio of the DPA and PtOEP molecules per NP and the NP dimensions could allow the fraction of PtOEP molecules that were not involved in the ET to be eliminated, or at least to be strongly reduced.

The presence of PtOEP molecules decaying with their natural lifetime underlines another relevant benefit of the dye embedding in the NPs, namely the shielding from the external surroundings, and, in particular, from molecular O_2. It is known that O_2 is a quencher of all of the phosphorescent emissions in organic molecules, representing a major drawback for standard organic bicomponent systems for up-conversion, which only work efficiently in oxygen-free solutions (O_2 concentration below 1 ppm), thus requiring sample preparation and manipulation in a glove-box.[33] As a consequence, their use is expensive, time consuming, and, in summary, not very appealing. In contrast, the shield offered by the NPs doesn't require any special care for sample preparation, allowing efficient up-conversion in such adverse conditions as the aqueous solutions used in the present work, or in air. It should be noted that the protection from oxygen is not only provided by the NP shell but also by the combination of the NPs and DTAB. Indeed, DTAB could be removed by several dialyses and the removal of surfactant could be easily followed by conductometry. No fluorescence was detected from the dialysates, indicating that the dyes remained in the cores of the NPs after dialysis. Once the DTAB was removed, the suspension was still highly fluorescent. However, once this suspension was drop-cast onto a glass slip, the up-converted PL quickly disappeared.

Regarding the fast, red PL-decay component ($\tau_2 = 8.9$), this arose from PtOEP molecules that were able to transfer their

excitation to the DPA. Indeed, the up-converted PL was not prompt, showing a rise time of $\tau_{rise} = 16.4$ μs (inset of Figure 3), which suggests that the DPA molecules were indirectly excited via ET from the PtOEP. In such a case, since the up-conversion arises from a bimolecular process, the DPA rise time is expected to be twice the decay time of the sensitizer emission. The experimental value of the DPA rise time was in good agreement with the expected value. The transfer efficiency (φ_{ET}) can be evaluated from $\varphi_{ET} = 1 - (\tau_{exp}/\tau_0)$.[38] By considering $\tau_{exp} = \tau_2$ and $\tau_0 = \tau_1$, a φ_{ET} value as high as 88% is obtained both for NPs in solution and in the cast films. The relative concentrations of PtOEP able (D) and unable (D') to transfer their excitation to the DPA can be determined directly from the ratio between the fast- and slow-component PL intensities at time $t = 0$.[38] In NP_{Susp}, $D/(D' + D) = 0.85$, which means that only few donors do not participate in the ET. Even considering this effect, the overall ET efficiency is still rather large: $\varphi_{ET} = 0.85 \times 0.88 \approx 75\%$. Similar findings were also obtained for suspensions with different NP concentrations (see Supporting Information), showing that, since the ET process was confined within each individual NP, its efficiency did not depend on the NPs' average separation distance. It should be noted that, since we performed time-resolved experiments with pulsed excitation at low repetition rates, the observed up-converted emission in these measurements arose from NPs containing more than one donor, where it was possible to excite more than one DPA with the same laser pulse via ET. Of course, this implies that the up-conversion efficiency was lower in the pulsed regime than under CW conditions (see Figure S7E, Supporting Information).

The performances of the PtOEP/DPA-doped NP_{Susp} and NP_{Film} were compared with those of the same dyes in a liquid polystyrene solution (2 g, 5% in tetrahydrofuran (THF), 1×10^{-3} M DPA and 1×10^{-4} M PtOEP). **Figure 4** shows the absolute DPA PL intensity upon CW excitation of PtOEP as a function of the absorbed photons per cm^2 in unit time (I_{exc}). Two parameters were evaluated: the excitation-power threshold (I_{th}) and the up-conversion quantum yield (QY). For the NPs, the absorbed flux was calculated by considering only the fraction of PtOEP
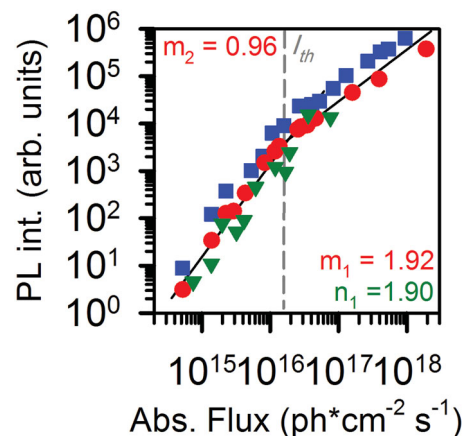

Figure 4. PL intensity at 435 nm under CW excitation at 532 nm as a function of the absorbed photon density of NP_{Film} (green triangles), NP_{Susp} (red circles) and a DPA (1×10^{-3} M)/PtOEP (1×10^{-4} M) polystyrene:THF solution (blue squares). For the NPs, the absorbed flux was calculated by considering only the fraction of PtOEP involved in ET to DPA.

FULL PAPER

involved in the ET to the DPA. The corresponding QY traces are shown in Figure S6E, Supporting Information. I_{th} corresponds to the power at which the spontaneous decay rate of the excited acceptor triplets equals the TTA rate. Above I_{th}, the overall efficiency of the systems becomes constant, reaching its maximum value.[14] Therefore, I_{th} determines if a system is suitable for solar applications or not.

It is easy to demonstrate that below I_{th} the up-converted PL increases as the square of the exciting power, while above this value the increase is only linear.[14] From an experimental point of view, I_{th} can be evaluated by plotting the up-converted PL as a function of the excitation power in a log–log plot (as in Figure 4) and looking at the excitation power at which the curves change their slope from two to one. For the NP_{Susp} sample (Figure 4, red circles), the calculated slopes are very close to the expected ones, being $m_1 = 1.92$ (quadratic versus I_{exc}) and $m_2 = 0.96$ (linear versus I_{exc}) for the low- and high-excitation-power-density regimes, respectively (for the NP_{Film} sample, because of the strong light scattering, the only regime carefully analyzable is the first one, where the calculated slope is $n_1 = 1.90$).[14] The corresponding I_{th} is 1.5×10^{16} ph cm^{-2} s^{-1} (5.6 mW cm^{-2}), not far from solar irradiance, considering that the width of the PtOEP absorption peak around 530 nm is about 15 nm. The measured value is almost equal to that of the prepared viscous solution (Figure 4, blue squares). These findings confirm the effectiveness of sensitized up-conversion within the NPs. As I_{th} did not change by tuning the NP concentration in the suspension (Figure S4E, Supporting Information), this demonstrates that each NP worked as a single up-converting unit. NP_{Susp} and NP_{Film} show the same QY (3.7% and 3.0% respectively) within experimental accuracy, the highest reported so far for up-converting systems in a solid environment.[42] Moreover, this value is not far from that obtained for the dyes in the THF:polystyrene solution (7.7%), without any dramatic efficiency drop moving from the solution to the solid state.[43,44]

The origin of the up-conversion QY difference in bulky rigid polymeric matrices and in NPs is not completely clear. Besides the oxygen shielding effect, we can draw some hypotheses: i) the local environment in the NP affects the DPA electronic structure and thus its intrinsic properties; ii) the interaction with the host matrix is too small to strongly reduce non-radiative mechanisms, determining the DPA triplet lifetime; iii) a latter possibility under investigation is the formation of coherent states delocalized on the whole DPA framework inside the NP.

3. Conclusions

In summary, sensitized photon up-conversion from 532 nm to 435 nm was successfully obtained in PtOEP/DPA-doped polymer NPs in both an aqueous suspension and drop-cast films. The I_{th} was as low as a few mW cm^{-2}, approaching solar irradiance, and the up-conversion efficiency of our solid samples was comparable to that of the corresponding dye solution. The dyes embedded within the NPs provided the crucial benefit of shielding both the chromophores from the external environment, preventing quenching by oxygen and suggesting a more-general employment of this material as a dye-protective shell. Finally, contrary to solution standard samples, in which the relative dye concentration is a crucial parameter, the observed kinetics were exactly the same for both NP_{Susp} and NP_{Film} (see Figure S2E, S3E, and S4E, Supporting Information). Each NP worked as single up-converting unit; thus, the obtained results offer the possibility of tuning the average dye concentrations in every solid system by varying the amount of embedded NPs, preventing typical concentration quenching effects such as self-absorption and allowing the manipulation of the material's optical density.

4. Experimental Section

NP Preparation and Doping: An aqueous suspension of nanoparticles (NPs) of 16 nm diameter was prepared by copolymerization in a microemulsion stabilized with the cationic surfactant DTAB (15 wt%) using a procedure described previously.[36,37] A microemulsion was prepared by progressive addition of a mixture of monomers (styrene/divinylbenzene/vinylbenzylchloride: 3.6/34.6/11.9 mmol) and 2,2-dimethoxy-2-phenylacetophenone (radical photoinitiator, 1.3 mmol) to 220 g of a 15 wt% solution of DTAB in demineralized water, under gentle magnetic stirring. The resulting microemulsion was degassed with nitrogen for 30 min and the polymerization was then carried out under white-light irradiation using two 60 W lamps, at room temperature under nitrogen, for 24 h. Chromatographic analysis indicated complete polymerization of all of the monomers. A stable, translucent, aqueous suspension of halobenzyl-functionalized nanoparticles was obtained. Cyclam-functionalized nanoparticles (NPs) were obtained by adding 1.30 g of cyclam (6.48 mmol) to 60 g of a crude suspension of the NPs. The mixture was stirred at room temperature for one week. The excess of cyclam was then removed by dialysis through a porous cellulose membrane (molecular-weight cut-off (MWCO) = 12 000 g mol^{-1}) towards an aqueous solution of DTAB (15 wt%). A stable, translucent aqueous suspension of cyclam-functionalized nanoparticles (NPs) was obtained.

Cyclam-functionalized nanoparticles were used in order to provide proper colloidal stability. The average particle diameter, deduced from dynamic light scattering (DLS), was 16 nm (polydispersity index (PDI) = 0.06); the particle content in the suspension was 4 wt%. 80 µL of a DCM solution containing DPA ([DPA] = 38.58 mmol L^{-1}) and PtOEP ([PtOEP] = 0.79 mmol L^{-1}) were added to 2 mL of an aqueous suspension of the nanoparticles. The resulting mixture was stirred at room temperature for 3 h in a capped sample tube. The tube was then uncapped and the solution was stirred for an additional 12 h to allow evaporation of the DCM. The suspension was filtered through a 0.2 µm MF-Millipore™ filter before use. The average numbers of molecules of DPA (50) and PtOEP (1) encapsulated per particle were deduced from the values of the absorbance of DPA at 374 nm ($\varepsilon = 15\,500$ mol^{-1} L cm^{-1} in DCM)[36,38] and of PtOEP at 380 nm ($\varepsilon = 290\,000$ mol^{-1} L cm^{-1} in toluene) and 535 nm ($\varepsilon = 174\,000$ mol^{-1} L cm^{-1} in toluene).[41]

In the mother solution, the concentration of NP was 31 µmol L^{-1} and the concentrations of DPA and PtOEP were: [DPA] = 1.55 mmol L^{-1} in solution, [PtOEP] = 0.031 mmol L^{-1} in solution; [DPA] = 38.75 µmol g^{-1} of polymer, [PtOEP] = 0.775 µmol g^{-1} of polymer; [DPA] = 38.75 mmol L^{-1} of polymer, [PtOEP] = 0.775 mmol L^{-1} of polymer; [DPA] = 0.117 µg g^{-1} of polymer, [PtOEP] = 1.065 ng g^{-1} of polymer.

Photophysical Studies: The optical-absorption measurements were carried out using a Cary Varian 50 Spectrometer with a bandwidth of 1 nm and using quartz cuvettes with an optical path of 0.1 cm (for the suspensions). For the steady-state PL measurements, a Coherent Verdi TEM00 CW laser at 532 nm (2.33 eV) was used as the excitation source, and a nitrogen-cooled charge coupled device (CCD) (Spex~2000) coupled to a polychromator (Triax 190 from J-Horiba) with a bandwidth of 0.5 nm was used for the signal detection. The time-resolved PL measurements involved excitation at 532 nm (2.33 eV) using the II harmonic of a Nd:YAG laser (Laser-Export Co. LCS-DTL-374QT), and detection in photon-counting mode using a Hamamatsu R943-02 photomultiplier connected to an Ortec 9353 multichannel scaler. Overall, the time resolution was better than 50 ns. Laser stray-light was reduced using a 532 nm notch filter. All of the measurements were performed at room

temperature (RT), and were corrected for the instrumental spectral response. None of the investigated samples showed any photoinduced degradation at the excitation power investigated. The up-conversion QY for the NP_{Susp} aqueous dispersion was measured using Rhodamine B as a fluorescence standard (see Figure S6E, Supporting Information), while for NP_{Film}, the yield was measured using an integrating sphere and the method reported by de Mello et al.[45]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

[1] A. Shalav, B. S. Richards, T. Trupke, K. W. Kramer, H. U. Gudel, *Appl. Phys. Lett.* **2005**, 86.

[2] T. Trupke, A. Shalav, B. S. Richards, P. Würfel, M. A. Green, *Sol. Energy Mater. Sol. Cells* **2006**, *90*, 3327.

[3] A. Shalav, B. S. Richards, M. A. Green, *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 829.

[4] X. F. Liang, X. Y. Huang, Q. Y. Zhang, *J. Fluoresc.* **2009**, *19*, 285.

[5] J. A. O'Brien, S. Rallabandi, U. Tripathy, M. F. Paige, R. P. Steer, *Chem. Phys. Lett.* **2009**, *475*, 220.

[6] Y. R. Shen *The Principles of Nonlinear Optics*, John Wiley & Sons, Hoboken, NJ, USA **2002**.

[7] S. Baluschev, T. Miteva, V. Yakutkin, G. Nelles, A. Yasuda, G. Wegner, *Phys. Rev. Lett.* **2006**, 97.

[8] R. R. Islangulov, F. N. Castellano, *Angew. Chem. Int. Ed.* **2006**, *45*, 5957.

[9] S. Balusachev, V. Yakutkin, T. Miteva, Y. Avlasevich, S. Chernov, S. Aleshchenkov, G. Nelles, A. Cheprakov, A. Yasuda, K. Mullen, G. Wegner, *Angew. Chem. Int. Ed.* **2007**, *46*, 7693.

[10] R. R. Islangulov, J. Lott, C. Weder, F. N. Castellano,. *J. Am. Chem. Soc.* **2007**, *129*, 12652.

[11] S. Baluschev, V. Yakutkin, G. Wegner, T. Miteva, G. Nelles, A. Yasuda, S. Chernov, S. Aleshchenkov, A. Cheprakov, *Appl. Phys. Lett.* **2007**, 90.

[12] S. Baluschev, V. Yakutkin, G. Wegner, B. Minch, T. Miteva, G. Nelles, A. Yasuda, *J. Appl. Phys.* **2007**, 101.

[13] A. Monguzzi, R. Tubino, F. Meinardi, *Phys. Rev. B: Condens. Matter* **2008**, 77.

[14] A. Monguzzi, J. Mezyk, F. Scotognella, R. Tubino, F. Meinardi, *Phys. Rev. B: Condens. Matter* **2008**, 78.

[15] R. E. Keivanidis, S. Baluschev, G. Lieser, G. Wegner, *ChemPhysChem* **2009**, *10*, 2316.

[16] J. Mezyk, R. Tubino, A. Monguzzi, A. Mech, F. Meinardi, *Phys. Rev. Lett.* **2009**, *102*, 4.

[17] F. Laquai, Y. S. Park, J. J. Kim, T. Basche, *Macromol. Rapid Commun.* **2009**, *30*, 1203.

[18] T. N. Singh-Rachford, J. Lott, C. Weder, F. N Castellano, *J. Am. Chem. Soc.* **2009**, *131*, 12007.

[19] A. A. Rachford, S. Goeb, F. N. Castellano, *J. Am. Chem. Soc.* **2008**, *130*, 2766.

[20] A. Kohler, H. Bassler, *Mater. Sci. Eng. R: Rep.* **2009**, *66*, 71.

[21] F. Laquai, G. Wegner, C. Im, A. Busing, S. Heun, *J. Chem. Phys.* **2005**, 123.

[22] P. B. Merkel, J. P. Dinnocenzo, *J. Lumin.* **2009**, *129*, 303.

[23] A. Monguzzi, R. Tubino, F. Meinardi, *J. Phys. Chem. A* **2009**, *113*, 1171.

[24] S. Ji, Dr. H. Guo, W. Wu, W. Wu, J. Zhao, *Angew. Chem. Int. Ed.* **2011**, *50*, 8283.

[25] S. Ji, W. Wu, W. Wu, Dr. H. Guo, J. Zhao, *Angew. Chem. Int. Ed.* **2011**, *50*, 1626.

[26] H. Sun, H. Guo, W. Wu, X. Liu, J. Zhao, *J. Chem. Soc. Dalton Trans.* **2011**, *40*, 7834.

[27] W. Wu, W. Wu, S. Ji, H. Guo, J. Zhao, *J. Chem. Soc. Dalton Trans.* **2011**, *40*, 9085.

[28] W. Wu, W. Wu, S. Ji, H. Guo, J. Zhao, *J. Chem. Soc. Dalton Trans.* **2011**, *40*, 5953

[29] W. Wu, H. Guo, W. Wu, S. Ji, J. Zhao, *J. Org. Chem.* **2011**, *76*, 7056.

[30] J. Sun, W. Wu, H. Guo, J. Zhao, *Eur. J. Inorg. Chem.* **2011**, 3165.

[31] L. Huang, L. Zeng, H. Guo, W. Wu, W. Wu, S. Ji, J. Zhao, *Eur. J. Inorg. Chem.* **2011**, DOI: 10.1002/ejic.201100777.

[32] L. F. M. L. Ciscato, D. Weiss, R. Beckert, E. L. Bastos, F. H. Bartoloni, W. J. Baader, *New J. Chem.* **2011**, *35*, 773.

[33] A. K. Bansal, W. Holzer, A. Penzkofer, T. Tsuboi, *Chem. Phys.* **2006**, *330*, 118.

[34] A. Monguzzi, R. Tubino, M. M. Salamone, F. Meinardi, *Phys. Rev. B: Condens. Matter* **2010**, 82.

[35] M. Frigoli, K. Ouadahi, C. Larpent, *Chem. Eur. J.* **2009**, *15*, 8319.

[36] F. Gouanve, T. Schuster, E. Allard, R. Meallet-Renault, C. Larpent, *Adv. Funct. Mater.* **2007**, *17*, 2746.

[37] R. Meallet-Renault, R. Pansu, S. Amigoni-Gerbier, C. Larpent, *Chem. Commun.* **2004**, 2344.

[38] J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Springer, Berlin, Germany **2008**.

[39] B. P. Lyons, A. P. Monkman, *Phys. Rev. B: Condens. Matter* **2005**, 71.

[40] R. C. Evans, P. Douglas, *Appl. Mater. Interfaces* **2009**, *1*, 1023.

[41] S. L. Pan, L. J. Rothberg, *J. Am. Chem. Soc.* **2005**, *127*, 6087.

[42] T. N. Singh-Rachford, F. N. Castellano, *Coord. Chem. Rev.* **2010**, *254*, 2560.

[43] Y. Y. Cheng, B. Fückel, T. Khoury, R. Clady, M. J. Y. Tayebjee, N. J. Ekins-Daukes, M. J. Crossley, T. W. Schmidt, *J. Phys. Chem. Lett.* **2010**, *1*, 1795.

[44] Y. Y. Cheng, T. Khoury, R. Clady, M. J. Y. Tayebjee, N. J. Ekins-Daukes, M. J. Crossley, T. W Schmidt, *Phys. Chem. Chem. Phys.* **2010**, *12*, 66.

[45] J. C. de Mello, H. F. Wittmann, R. H. Friend, *Adv. Mater.* **1997**, *9*, 230.