A general approach for non-coherently excited annihilation up-conversion: transforming the solar-spectrum

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Abstract. We demonstrate up-conversion with an external quantum yield of 3.2% realized at ultra-low excitation intensities ($\sim$0.1 W cm$^{-2}$). The bimolecular up-conversion process in our systems relies on the presence of a metastable triplet excited state, and thus has substantially different photophysical characteristics when compared with the other known methods for photon up-conversion (two-photon absorption, parametric processes, second harmonic generation, sequential multiphoton absorption, etc). Thus, we state the general requirements for the materials’ parameters of the couple sensitizer/emitter for obtaining triplet–triplet annihilation up-conversion. One of the applications we suggest for active materials compositions is the achievement of energetically stepwise up-conversion of the terrestrial solar spectrum towards blue wavelengths: as such they could be used for improving the efficiency of the solar cells. Up-conversion with non-coherent excitation by sunlight with wavelengths between 550 and 700 nm is demonstrated.

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1. Introduction and background

A direct increase of the spectral brightness of the short wavelength region of the solar spectrum by using photons from the longer wavelength region remains today a very considerable challenge. Here, we suggest a stepwise up-conversion process transforming the near infra red part of the terrestrial Sun emission towards the blue wavelengths. This we have realized by up-conversion fluorescence in a two-component organic system. The examples of up-conversion described in the literature until now, i.e. the generation of photons, notably spectrally blue shifted to the wavelength of the excitation photons, by simultaneous or sequential absorption of two or more photons with lower energy, has been commonly associated with the use of coherent light sources (lasers). The formidable limitations of these existing methods include the high light intensities (usually, in the order of kW cm$^{-2}$ and MW cm$^{-2}$ [1–4]) and the very high excitation spectral power densities in the order of 10 W nm$^{-1}$ required: these extreme conditions cannot be reached through means of non-coherent light sources, and especially not with the Sun.

To mention but one of the many possible applications of an efficient and high-energy photon up-conversion would be its use as an elegant way to increase the efficiency of various solar cells [5, 6]. Quite a few materials used in organic solar cells have higher absorption coefficient in the blue region than in either the green and red regions; however, it is these regions where the maximum solar spectral irradiance is found. We thus suggest that the up-converter could be located behind the solar cell to enable the more efficient harvesting of the green and red region of the solar irradiance and is furthermore fully electronically insulated from the solar cell.

The process of photon up-conversion based on triplet–triplet annihilation (TTA) has been observed for a broad variety of metal complexes, serving as sensitizer and emitter molecules. Recently it has been shown that metallated macrocycles (MMs) such as platinum, palladium, zinc, and copper octaethylporphyrins [7, 8], Ru(II) diimine- and iridium phenylpyridine-metal-to-ligand charge transfer complexes [9, 10] can serve as sensitizers in this bimolecular up-conversion process. The characteristic up-converted fluorescence was observed from emitting molecules such as polyfluorenes [7], polyspirobifluorene–anthracene copolymer [11], palladium-porphyrin end-capped [12] ladder-type poly(paraphenylene) and anthracene derivatives [9, 10, 13]. Furthermore, the up-conversion process was not only investigated in solutions [9, 10, 13], but also in solid amorphous films [7, 8]. It has also been studied in surface-plasmon geometry [14]. All of these numerous examples indicate that indeed the TTA supported bimolecular up-conversion is a universal phenomenon rather than a peculiarity for a restricted number of active molecules. If the required overlap of the triplet bands of the sensitizer and emitter molecules is fulfilled, and a large difference in the intersystem crossing (ISC) rates for the sensitizer and emitter molecules is present, then certainly this
Figure 1. The proposed energetic scheme of a TTA supported up-conversion process. The dotted path represents the transfer of excitation energy by up-conversion in the anthracene derivative/MM system. For instance, for the up-conversion couple BPEA/PdPh₄TBP, then the energy of the excitation photons is 1.98 ± 0.08 eV, whereas the energy of the emitted photons is 2.5 ± 0.1 eV. It is required that the energetic positions of the triplet manifold of both the sensitizer and emitter have a spectral overlap.

process should be observed for many other molecules known as materials capable of electro-generated chemiluminescence [15].

The process of photon up-conversion, based on TTA in a multi-molecular system is to be considered as an inherently connected chain of three processes which have already been studied in the past. The first process in this chain is ISC, which is strongly enhanced by the spin–orbit coupling to the metal centre of MM sensitizer molecules [16, 17]. The second process [18] in the chain is the transfer of the excitation of the sensitizer triplet to the emitter triplet (TTT). The third process is the subsequent TTA, which in our system occurs mostly between emitter molecule triplets [19]–[21].

The fundamental advantage of the TTA supported bimolecular up-conversion process is its inherent independence on the coherence of the excitation light [22]. The optical excitation of the active system occurs by resonant single photon absorption: consequently, the efficiency of the up-conversion process depends only on the material’s properties but does not in any way depend upon the coherence of the photons used for excitation. Yet another principal advantage of the studied up-conversion process is the extremely low spectral power density of the excitation source required for effective fulfilling of the up-conversion chain of events. For example, spectral power densities as low as 200 µW nm⁻¹ are sufficient for effective up-conversion.

2. Materials and methods

A schematic representation of the process of the photon up-conversion under investigation is shown in figure 1. The efficient ISC within the sensitizer molecules (for instance, the probability is almost 1 for the metallated porphyrins [23]) ensures a very efficient population of the sensitizer triplet level via single photon absorption.
The sensitizer triplet states with their relatively long life times (which exceed several tens of microseconds in the case of the porphyrins discussed in this work) serve as energy reservoirs. Beyond the trivial depopulation channels for these triplet states—which include radiative decay and non-radiative decay—there is an additional less trivial decay channel. This channel is characterized by a transfer of the triplet excitation of the MM directly to the triplet state of the emitter molecule. The efficiency of this triplet–triplet transfer is predetermined by the extent of overlap of the sensitizer and emitter triplet bands. The very weak tendency for ISC of the emitter molecules (the probability has values between 0.02 and 0.09 for various anthracene derivatives [15]) substantially prohibits the depopulation of the excited emitter triplet states via phosphorescence and thus stores the created triplet population of the emitter for the process of TTA. As a consequence of the weak ISC-probability for the emitter molecules a dense populated ensemble of emitter molecules in the excited triplet state is created. The probability for TTA mostly between the excited emitter triplet states grows significantly. As a result of the homo-TTA, some emitter molecules are excited to a singlet state and the characteristic fluorescence is observed. There is a non-zero probability for observing a hetero-TTA between the excited triplets of the sensitizer and the emitter molecules. Taking into account the large difference between the concentration of the sensitizer and emitter molecules necessary for efficient up-conversion, one can conclude that the impact of the hetero-TTA on the total up-conversion signal is negligible.

The extension of the \(\pi\)-conjugated system in the metallated porphyrins by annulated aromatic rings results in a noticeable red shift [24] in the absorption and emission spectra. Our interest in particular porphyrins, such as tetrabenzoporphyrins [25] and tetranaphthophorphyrins [26], arises from their ability to expand the excitation spectra for up-conversion deep into the red region of the visible spectrum. Recently, metallated porphyrins with extremely planar geometries [27] were synthesized.

The structures of the investigated sensitizers in this work are shown in figure 2: (1a), 2,7,8, 12,13,17,18-octaethylporphyrin palladium (PdOEP) was purchased from Porphyrin Systems Inc.; (2a), meso-tetraphenyl-tetrabenzoporphyrin palladium (PdPh\(_4\)TBP) was purchased from Sigma-Aldrich. The meso-tetraphenyl-octamethoxide-tetranaphtho[2,3]porphyrin palladium (PdPh\(_4\)OMe\(_8\)TNP) was synthesized (3a) in our group. The structures of the emitters are shown in figure 2: (1b), 9,10-diphenylanthracene (DPA); (2b), 9,10-bis(phenylethynyl)anthracene.
Figure 3. (a) Normalized absorption spectra of the sensitizers—PdOEP (navy line), PdPh₄TBP (dark cyan line) and PdPh₄OMe₈TNP (orange line) in toluene solutions. (b) Normalized absorption spectra of the corresponding emitters—DPA (navy line) BPEA (dark cyan line) and BPEN (orange line) in toluene solution. For clarity, the colours of the absorption spectra of the corresponding sensitizer/emitter couples are the same.

(BPEA); and (3b), 9,10-bis(phenylethynyl)naphthacene (BPEN) were all purchased from Sigma-Aldrich. All compounds were used as received.

3. Results and discussion

The absorption spectra of the sensitizers investigated in this work are shown in figure 3(a), as follows: PdOEP (navy line), PdPh₄TBP (dark cyan line) and PdPh₄OMe₈TNP (orange line). All sensitizers have significant absorption in their Q-bands. As shown in figure 3(b), the absorption of the corresponding emitters, as follows, DPA (navy line), BPEA (dark cyan line) and BPEN (orange line)—is negligible at wavelengths close to the Q-band absorption of the corresponding sensitizer. Consequently, neither DPA and BPEA nor BPEN—singlet emission can be observed, when these emitters are exposed to the broadband non-coherent light centred at 550, 630 or 700 nm, respectively in their pure solutions.

The dynamic properties of the TTA supported up-conversion process in sensitized solutions containing DPA/PdOEP ((a) excited at λ = 532 nm), BPEA/PdPh₄TBP ((b) excited at λ = 635 nm) and BPEN/PdPh₄OMe₈TNP ((c) excited at λ = 695 nm) are shown in figure 4. For the time-resolved measurements, the excitation laser light was suppressed by more than a
Figure 4. Streak camera images of the time-evolution of the annihilation up-conversion fluorescence of DPA/PdOEP (a); BPEA/PdPh₄TBP (b) and BPEN/PdPh₄OMe₈TNP (c). A CCD-camera images of the up-converted fluorescence inside 1 mm thick cuvettes (frontal excitation) for the systems: DPA/PdOEP (e), BPEA/PdPh₄TBP (f) and BPEN/PdPh₄OMe₈TNP (g). For the CCD-images the excitation intensities are less than 150 mW cm⁻² and no blocking filters were used.

factor of 10⁵ by using notch filters, designed for λ = 532 nm and 635 nm and a shortpass edge filter with a cutting wavelength of λ = 680 nm. The molar concentration of the sensitized solutions was as follows: sensitizer/emitter—10⁻⁴ M/10⁻³ M and was the same for each couple. The duration of the laser pulse was 1 ms with slopes of less than 1 μs and an excitation intensity of 10 W cm⁻². The streak-camera images (Hamamatsu C5680, single pulse regime) represent about the first 60 μs of the excitation pulse, together with the following 60 μs after the termination of the pulse. It has to be pointed out that the up-conversion fluorescence rise-time depends strongly on the pump intensity: with increasing pump intensities the rise-time drastically decreases. This phenomenon has also been observed and discussed in [22].

To continue, thus the up-conversion fluorescence of the emitter molecules has a rise-time varying from about 8 μs to about 30 μs (at a given excitation intensity). This difference in the rise-times represents the time necessary for a transfer of the triplet population from sensitizer-triplet to emitter-triplet level and the filling of the emitter triplet reservoir, together with other process characteristic parameters, such as triplet–triplet overlap and the decay rate of the non-emissive decay channels for the excited sensitizer molecules. All these parameters are specific for each sensitizer/emitter couple. The decay dynamics of the up-conversion fluorescence after termination of the pump pulse is also shown in figure 4 (on the right-hand side of (a), (b) and (c)). The decay time of the annihilation up-conversion fluorescence ranges from about 10 μs (in the case of DPA) up to about 30 μs (in the case of BPEN) and characterizes the strength of the TTA between the emitter molecules. As a general rule, longer decay times correspond to photon up-conversion with lower quantum efficiencies.

We present here, for the first time, up-conversion fluorescence obtained by ultra-low excitation intensities of 150 mW cm⁻² or lower. The excitation power was in the order of ~10 mW, and the excitation spot area exceeded 0.1 cm². In figure 4 are shown the
CCD-camera images of fluorescence excited in the up-conversion regime, as follows: for the couple DPA/PdOEP (e)—$\lambda = 532$ nm (Nd: YAG, second harmonic), 50 mW cm$^{-2}$; for BPEA/PdPh$_4$TBP (f)—$\lambda = 635$ nm (single mode diode laser), 70 mW cm$^{-2}$; for BPEN/PdPh$_4$OMe$_8$TNP (g)—$\lambda = 695$ nm (single mode diode laser), 150 mW cm$^{-2}$.

From a practical point of view, the external quantum efficiency of the up-conversion process is certainly of decisive importance. The classical definition for quantum yield (the JUPAC definition) is stated and devised for a single species. Therefore, it is not entirely directly applicable to more complicated multi-species up-conversion processes such as TTA-supported up-conversion in multicomponent organic systems. Nevertheless, that said, the main benefit of using such a rigorous quantum yield definition arises from the clear and transparent evaluation for the reader of the application potential of the TTA up-conversion.

For estimation of the quantum yield of the TTA up-conversion, we accepted the methodology commonly used for the determination of fluorescence quantum yields of single emitters $[28]$. As such, we consider the TTA up-conversion as a one-step process with ‘absorption’—corresponding to the absorption of the MMs molecules and ‘emission’—corresponding to the emission of the anthracene derivatives. The particulars of these processes, happening in the ‘up-conversion black-box’, are neglected. After this simplification of the TTA up-conversion, we compare the system under study to a reference standard of known quantum efficiency, together with other measurable parameters. The unknown quantum yield ($Q_X$) of the fluorescence, excited in the up-conversion regime is thus presented in equation (1):

$$Q_X = Q_R (E_X/E_R) (h\nu_X/h\nu_R) (n_X^2/n_R^2) (I_R/I_X) (A_R/A_X).$$

(1)

Here $E$ is the emission integral, $I$ is the light intensity at the excitation wavelength, $A$ is the absorbance of the solution at the excitation wavelength, $n$ is the refractive index of the solvent at the emission wavelength, $h\nu$ is the energy of the excitation photons. The subscripts $X$ and $R$ respectively refer to the up-conversion system and to the optical standard. In order to minimize the influence of the boundary effects, caused by the diffusion of excited states on the annihilation controlled process of up-conversion, we used for the excitation a collimated beam with diameter of $3.9 \times 10^{-3}$ m and an ultra-low excitation intensity of 80 mW cm$^{-2}$.

The quantum yield of the TTA supported process of photon up-conversion is shown in figure 5 for the couple BPEA/PdPh$_4$TBP. In this case, the quantum yield is an integral parameter describing the efficiency of a chain of events, starting with the absorption of a single photon in the Q-band of the sensitizer. The complexity of the processes studied is reflected by the dependence of the quantum yield on the emitter molar concentration (at a constant sensitizer molar concentration of $10^{-4}$ M, figure 5(a)) and also by the sensitizer molar concentration (at constant molar ratio of sensitizer/emitter $\sim 1/10$, figure 5(b)). The highest up-conversion quantum yield of 3.2% was observed for $2 \times 10^{-5}$ M PdPh$_4$TBP and $2 \times 10^{-4}$ M BPEA.

The bimolecular up-conversion relies on the presence of the relatively long-lived triplet state of the sensitizer molecule. Another well-known fact is that oxygen molecules are renowned to be very effective quenchers of the excited triplet states of the MMs, such as the porphyrins—see for example $[23]$. This predetermines the strong dependence of the up-conversion efficiency even upon a residual oxygen concentration in the range of parts per million (ppm). So, correspondingly, all the solutions investigated were prepared from degassed toluene and sealed in a nitrogen-filled glove box. A glove box filled with argon would further improve the durability of the sealed samples, because the heavier argon would be less likely to be replaced by any ingressing oxygen. Therefore, the reported up-conversion efficiency could be treated as
Figure 5. Dependence (a) of the quantum yield of the up-conversion on the relative concentration of the emitter at a constant concentration ($10^{-4}$ M) of the sensitizer. Dependence (b) of the quantum yield of the up-conversion on the sensitizer concentration at constant molar ratio ($\sim 1/10$) of sensitizer/emitter.

As the optical reference standard a $10^{-5}$ M toluene solution of BPEA excited at $\lambda = 407$ nm with quantum yield of 85% [28] was used.

an estimation value only for the certain sensitizer/emitter couple and for the given sample preparation techniques, but not as an absolute efficiency for this bimolecular up-conversion process. In summary, the efficiency can certainly be further optimized for specific application needs.

Consequently, through attentive sample preparation, comprising of adjusting the sensitizer/emitter couples we could then demonstrate the achievement of up-conversion photoluminescence excited by using ultra-low intensity (as low as 1 W cm$^{-2}$) and very low spectral brightness (excitation spectrum width: $\Delta \lambda \sim 40$ nm full width at half maximum (FWHM)) non-coherent sunlight in energetically stepwise situated systems. As an excitation source we used: the green (around 550 nm, figure 6(a), the green line), the red (around 630 nm, figure 6(a), the red line) and near infrared (around 700 nm, figure 6(a), the dark red line) part of the terrestrial Solar spectrum, respectively. A Dobsonian telescope (12" Lighbridge, Meade Ins. Corp.) was used to collect the sunlight and couple it into an optical fibre (Multimode, 1000 $\mu$m, NA = 0.48, Thorlabs Inc.). Firstly, in order to reduce the thermal stress for the optical elements, the infrared tail of the solar spectrum (wavelengths longer than 750 nm) was rejected through the use of a large size (12") interference filter (AHF Analysentechnik GmbH) before focusing on to the
Figure 6. Up-conversion fluorescence spectrum of DPA/PdOEP ((b), navy blue line), BPEA/PdPh₄TBP ((b), dark cyan line) and BPEN/PdPh₄OMe₈TNP ((b), orange line) in solution, excitation intensity 1 W cm⁻², excited by a portion of the Solar spectrum ((a), grey line)—near 550 nm ((a), green line), 630 nm ((a), red line) and 700 nm ((a), dark red line), respectively. A CCD-camera image of the up-converted fluorescence inside a 1 cm cuvette, for the systems DPA/PdOEP, BPEA/PdPh₄TBP and BPEN/PdPh₄OMe₈TNP, excited with the corresponding part of the Sun’s spectrum, 1 W cm⁻². For the CCD-images no blocking filters were used.

face of the optical fibre. Finally, the necessary excitation sunlight band was selected by using a broadband interference filter at the output of the optical fibre. The light intensity at the focal spot was in the order of 1 W cm⁻².

The cw-fluorescence spectra excited in the regime of up-conversion are shown in figure 6(b) for systems consisting of $1 \times 10^{-3}$ M DPA/1 $\times 10^{-4}$ M PdOEP (navy blue line), $1 \times 10^{-3}$ M BPEA/1 $\times 10^{-4}$ M PdPh₄TBP (dark cyan line) and $1 \times 10^{-3}$ M BPEN/1 $\times 10^{-4}$ M PdPh₄OMe₈TNP (orange line), respectively. The emission spectra were registered by an optical fibre-spectrometer in the lateral direction without using any further blocking optical filters.
The integral non-coherent excitation intensity was 10 mW and the excitation spot diameter \((1/e) \sim 1.8 \times 10^{-3} \text{ m}\), e.g. the excitation intensity was as low as 1 W cm\(^{-2}\). It is important to notice that the phosphorescence of the sensitizers (not shown) is almost completely quenched in all cases. Taking into account the relatively broad excitation spectrum \((\Delta \lambda \sim 40 \text{ nm FWHM})\) and the ultra-low excitation power of 10 mW, one can estimate the spectral power density of the excitation source \((\sim 250 \mu \text{W nm}^{-1})\) sufficient for observing efficient up-conversion.

The enormous and wide-ranging application potential of the studied up-conversion process arises from the drastically decreased requirements of the excitation light source parameters. The efficiency of the TTA up-conversion does not depend on the spatial distribution of the wavevectors of the excitation light: the linear absorption in the sensitizer does not depend on the entrance angle of the excitation photons. Furthermore, excitation photons with time mismatch of up to 20 \(\mu\text{s}\) (this mismatch time depends upon the lifetime of the excited emitter triplet states), difference of energies of up to 0.15 eV regarding the central wavelength (this energy difference depends upon the width of the sensitizer absorption spectrum) and additionally, absorption locations spatially separated by more than 10 \(\mu\text{m}\) (this distance depends upon the specific diffusion coefficients of the sensitizer and emitter molecules) will participate in the TTA-supported up-conversion process with nearly the same efficiency. So, all the inherently fundamental limitations of the optical source parameters, reducing the range of the possible light sources, able to excite efficiently up-conversion optical processes only to laser sources [1], are disestablished.

Further, we would like to point out that the emission band of BPEN (figure 6(b), orange line) coincides very well with the absorption band of PdPh\(_4\)TBP (figure 3(a), dark cyan line), and furthermore that the emission band of BPEA (figure 6(b), dark cyan line) overlaps well with the absorption band of PdOEP (figure 3(a), navy blue line). The intensity needed for efficient up-conversion fluorescence lies in the range of one Sun. Therefore, we would like to conclude that a cascade up-conversion of the solar spectrum by TTA annihilation up-conversion appears to be very feasible indeed.

4. Conclusion

We demonstrate a general approach for non-coherently excited photon up-conversion. The required conditions for effective TTA supported up-conversion have been established. At first, a strong absorption in the red-shifted sensitizer band (Q-band), together with the very high ISC-rate of the sensitizer ensures a densely populated sensitizer triplet ensemble. Next, the existence of a broad transparency window between the Soret-band and Q-band of the sensitizer guarantees a low degree of re-absorption and predetermines the maximal energetic shift of the up-conversion emission. Furthermore, a strong overlap of the triplet bands of the sensitizer and emitter molecules, together with a large difference in the ISC rates for the sensitizer and emitter molecules is necessary for building-up a high-populated ensemble of emitter triplets. The best material combinations are when the ISC rate of the sensitizer approaches 1 and the emitter quantum yield is as close to 1 as possible, together with broad transparency window at the sensitizer absorption band and nearly coinciding emitter absorption band and Soret-band of the sensitizer.

MMs and anthracene derivatives satisfy these conditions. Achieving a practicable resolution to these requirements allowed us to demonstrate quantum yields of the annihilation process.
assisted up-conversion process for the couple PdPh₄TBP/BPEA to be as high as 3.2% with an excitation intensity of 80 mW cm⁻².

We demonstrate experimentally photon up-conversion by using as excitation source various bands of the terrestrial solar spectrum. This, together with the inherent independence of the used TTA-assisted process on the coherence of the excitation source, demonstrates the possibility for a step-wise up-conversion of the terrestrial solar spectrum towards blue wavelengths. With these results, we prove a general strategy for photon up-conversion, excited within a broad spectral range from green (λ = 530 nm) down to near infra red (λ = 720 nm).

References

[1] Shen Y R 2002 The Principles of Nonlinear Optics (Berlin: Wiley)
[2] Boyer J-C, Cuccia L A and Capobianco J A 2007 Synthesis of colloidal upconverting NaYF₄: Er³⁺/Yb³⁺ and Tm³⁺/Yb³⁺ monodisperse nanocrystals Nano Lett. 7 847–52
[3] Suyver J F, Aebischer A, Biner D, Gerner P, Grimm J, Heer S, Krämer K W, Reinhard C and Güdel H U 2005 Novel materials doped with trivalent lanthanides and transition metal ions showing near-infrared to visible photon upconversion Opt. Mater. 27 1111
[4] Auzel F 2004 Upconversion and anti-Stokes processes with f and d ions in solids Chem. Rev. 104 139
[5] Würfel P 2000 Physik der Solarzellen (Leipzig: Spektrum Akademie Verlag)
[6] Trupke T, Shalava A, Richards B S, Würfel P and Green M A 2006 Efficiency enhancement of solar cells by luminescent up-conversion of sunlight Solar Energy Mater. Solar Cells 90 3327–38
[7] Yasuda A, Nelles G, Miteva T, Keivanidis P E, Lupton J and Balouchev S 2005 Composition for photon-energy up-conversion US Patent No US2005056815
[8] Keivanidis P E, Baluschev S, Miteva T, Nelles G, Scherf U, Yasuda A and Wegner G 2003 Up-conversion in polyfluorene doped with metal (II)-octaethyl Adv. Mater. 15 2095
[9] Islangulov R R, Kozlov D V and Castellano F N 2005 Low power upconversion using MLCT sensitizers Chem. Commun. 30 3776–8
[10] Zhao W and Castellano F N 2006 Upconverted emission from pyrene and di-tert-butylpyrene using Ir(ppy)₃ as triplet sensitizer J. Phys. Chem. A 110 11440–5
[11] Laquai F, Büsing A, Im C, Heun S and Wegner G 2005 Efficient upconversion fluorescence in a blue-emitting spirobi fluorene-anthracene copolymer doped with low concentrations of Pt(II)octaethylporphyrin J. Chem. Phys. 123 074902
[12] Baluschev S, Jacob J, Avlasevich Y S, Keivanidis P E, Miteva T, Yasuda A, Nelles G, Grimsdale A C, Müllen K and Wegner G 2005 Enhanced operational stability of the up-conversion fluorescence in films of palladium-porphyrin end-capped poly(pentaphenylene) ChemPhysChem 6 1250–3
[13] Baluschev S, Miteva T, Minch B, Yakutkin V, Nelles G, Yasuda A and Wegner G 2007 Two pathways for photon up-conversion in model organic compound systems J. Appl. Phys. 101 023101
[14] Baluschev S, Yu F, Miteva T, Ahl S, Yasuda A, Nelles G, Knoll’ W and Wegner G 2005 Metal enhanced up-conversion fluorescence: effective triplet–triplet annihilation near silver surface Nano Lett. 5 2482
[15] Armstrong N R, Wightman R M and Gross E M 2001 Light-emitting electrochemical processes Annu. Rev. Phys. Chem. 52 391–422
[16] Kasha M 1950 Characterization of electronic transition in complex molecules Discuss. Faraday Soc. 9 14–9
[17] Fulton R L and Gouterman M 1961 Vibronic coupling. 1. Mathematical treatment for 2 electronic states J. Chem. Phys. 35 1059
[18] Terenin A and Ermolaev V 1956 Sensitized phosphorescence in organic solutions at low temperature—energy transfer between triplet states Trans. Faraday Soc. 52 1042–52
[19] Porter G and Windsor M W 1954 Studies of triplet state in fluid solvents Discuss. Faraday Soc. 17 178
[20] Parker C A, Hatchard C G and Joyce T A 1965 Selective and mutual sensitization of delayed fluorescence Nature 205 1282
[21] Avakian P and Merrifie R E 1968 Triplet excitons in anthracene crystals—a review Mol. Cryst. 5 37
[22] Baluschev S, Miteva T, Yakutkin V, Nelles G, Yasuda A and Wegner G 2006 Up-conversion fluorescence: non-coherent excitation by sun-light Phys. Rev. Lett. 97 143903
[23] Pope M and Swenberg C 1982 Electronic Processes in Organic Crystals (Oxford: Clarendon)
[24] Kadish K and Smith K M (ed) 2003 The Porphyrin Handbook (Berlin: Elsevier)
[25] Finikova O S, Chernov S Y, Cheprakov A V, Filatov M A, Vinogradov S A and Beletskaya I P 2003 New selective synthesis of substituted tetrabenzoporphyrins Dokl. Chem. 391 222–4
[26] Finikova O S, Cheprakov A V, Carroll P J and Vinogradov S A 2003 Novel route to functionalized tetraaryl-2,3]naphthaloporphyrins via oxidative aromatization J. Org. Chem. 68 7517–20
[27] Finikova O S, Cheprakov A V and Vinogradov S A 2005 Synthesis and luminescence of soluble meso-unsubstituted tetrabenzo- and tetranaphtho[2,3]porphyrins J. Org. Chem. 70 9562–72
[28] Hanhela P J and Paul D B 1984 Evaluation of fluorescent materials for colour control of peroxylate chemi-luminescence. 4 Fluorescence quantum yields of some phenyl and phenylethynyl aromatic-compounds Aust. J. Chem. 37 553–59