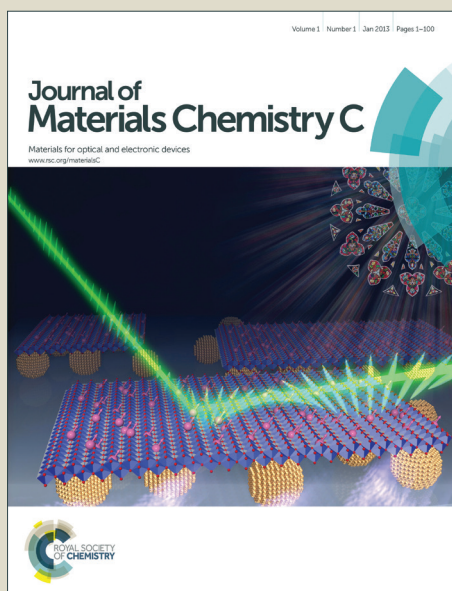


Journal of Materials Chemistry C

Accepted Manuscript



This article can be cited before page numbers have been issued, to do this please use: C. Ye, B. Wang, X. Wang, P. Ding, X. Tao, Z. Chen, Z. Liang and Y. Zhou, *J. Mater. Chem. C*, 2014, DOI: 10.1039/C4TC00791C.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ARTICLE

O/w microemulsion: An effective medium for triplet-triplet annihilated upconversion with efficient triplet acceptors

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2014,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Changqing Ye,^{a,§} Bao Wang,^{a,§} Xiaomei Wang,^{a,*} Ping Ding,^a Xutang Tao,^b
Zhigang Chen,^a Zuoqing Liang,^a Yuyang Zhou^a

The oil-in-water (o/w) microemulsion containing bimolecular system of acceptor (9,10-dinaphthylanthracene) and sensitizer (Pd(II)tetratolylporphyrin), i.e., upconverted o/w microemulsion, was firstly reported for the triplet-triplet annihilated upconversion (TTA-UC) by temperature effect. The correlations between structure/upconversion performance of three 9,10-dinaphthylanthracenes doped with Pd(II)tetratolylporphyrin were investigated. Under the excitation of ultralow power density at 60 mW·cm⁻², the upconverted o/w microemulsion emits green-to-blue upconversion and the efficiency (Φ_{UC}) increase is accompanied by the temperature increase. The maximum Φ_{UC} value for the upconverted o/w microemulsion was obtained as high as 33.12% that is comparable to the counterpart in pure organic solvent. Very importantly, it is no need for the upconverted o/w microemulsion to deaerate, which is of critical importance for the application such as upconversion-powered photoelectrochemistry. To the best of our knowledge, the current study represents the simple approach to obtain high TTA-UC without degassing anymore.

Introduction

Two-photon absorption (TPA) is a nonlinear optical process¹⁻³ that a molecule simultaneously absorbs two photons via virtual state toward the excited state and usually results in photon-upconversion. Although such TPA-based upconversion exhibits valuable potential applications such as upconversion lasing,⁴ two-photon polymerization⁵ and photodynamic therapy,^{6,7} it always needs very high excitation intensity as high as hundreds of MW~GM·cm⁻² (one million times as large as solar energy)⁸ that leads to the serious application limitation. Alternatively, another photon-upconversion mechanism has already been paid much attention recently, which is called triplet-triplet annihilation (TTA) upconversion.^{9, 10} TTA upconversion (TTA-UC) is also a nonlinear optical process¹¹ which involves in a bimolecular system (i.e., sensitizer/acceptor). TTA-UC undergoes a series of multiple quantum processes:¹² that is, i) the sensitizer firstly absorbs one photon to the excited singlet state and goes across its triplet excited state by intersystem crossing (ISC); ii) then the triplet-triplet energy transfer (TTT) occurs from the sensitizer to acceptor; and then two triplet acceptors actualize

the triplet-triplet annihilation (TTA) with the result that the photon-upconversion produces. The most important thing is that such TTA upconversion can be obtained at very low excitation intensity (less than 100 mW·cm⁻², solar energy is enough),^{13, 14} which would bring about many practical applications such as photovoltaics,¹⁵ photocatalysis,¹⁶ photodynamic therapy of cancer¹⁷ and display¹⁸ as well as the solar cells.¹⁹ For example, in the single-junction solar cell the unabsorbed long-wavelength transmission light can be efficiently upconverted into absorbable photons through upconversion materials which makes its theoretical efficiency reach 1.33-folds increase in comparison with that without upconversion materials.^{19, 20} However, the TTA upconversion materials work efficiently only to shorter wavelengths ≤ 750 nm,²¹ Moreover, since TTA-UC relies exclusively on the efficient generation of the triplet excited states of both sensitizer and acceptor, dissolved O₂ can strongly annihilate these formed triplets.^{22, 23} So, the medium for upconversion must be devoid of oxygen to prevent triplet-state quenching, which is absolutely not ideal for the most TTA-UC

applications. Although lots of efforts have been made to achieve TTA-UC in the aerated environment by embedding chromophores in rubbery polymeric matrixs,^{24–26} encapsulating chromophores with rigid polymer shell,^{27–30} loading chromophores into silica nanoparticles³¹ as well as even incorporating the upconverting dyes in micellar carriers,³² all of these have shown some intrinsic limitations of either the complicated preparation processes or very low UC-efficiency (less than 6% at the excitation intensity of 100 mW·cm⁻²). Of the mentioned techniques, micro-emulsification is a simple method, widely used for encapsulation in micelles by surfactants to produce nanoparticles including metals,³³ semiconductor nanoparticles³⁴ and polymer-based TTA up-conversion nanoparticles.³⁵ However, few reports have published to obtain high TTA-UC efficiency in o/w microemulsion with temperature effect to our knowledge.

In this paper, we have demonstrated for the first time that o/w microemulsion can act as an effective medium for the TTA-UC performance by temperature tuning. This o/w (oil-in-water) microemulsion using nonionic surfactant as emulsifier can be reversibly converted into w/o (water-in-oil) microemulsion with a phase inversion temperature (PIT).^{36, 37} That is, in the upconverted o/w microemulsion, the nanometer-sized droplets of oil containing sensitizer/acceptor pair can disperse in water-rich continuous phase at room temperature. When the temperature is increased, the nanometer-sized droplets of water conversely dispersed in oil-rich continuous phase wherein the soluble sensitizer/acceptor would freely collide with each other. As a result, the enhanced upconversion efficiency (Φ_{UC}) in microemulsion medium could be comparable to the counterpart in pure organic solvent. Besides the obvious advantages offered by upconverted o/w microemulsion such as absence of toxic solutions, easy to fabricate, being inexpensive and stable; the most important thing is that it presents high upconversion efficiency (e.g., Φ_{UC} = 33.12 % at the excitation intensity of 60 mW·cm⁻²) without the need of deaerating, which is of critical importance from a practical point of view.

Experimental

All chemicals were purchased from Aldrich or Acros Chemical Co. and were used without any further purification. The synthesis details of three 9,10-dinaphthylanthracenes (DNAME, DNACI and DNACN) (Figure 1) are found in the supporting information section.

2.1 Preparation of o/w microemulsion

Sensitizer (0.12 mM) and acceptor (1.2~48 mM) stock solutions were prepared prior to the experiment by dissolving in toluene and kept in dark prior to use.

To get the transparent upconverted oil-in-water (o/w) microemulsion, 2 mL of stock solutions were added into the deionized water (18 mL) in the presence of Tween-20 (10 mL) at room temperature under stirred condition and N₂ atmosphere. Thus, a series of the upconverted o/w microemulsions were obtained with diameters of 40~60 nm in size (Figure S1 in supporting information section).

2.2 Characterization and measurements

Melting points (m.p.) were recorded on an X-5 melting point measurement instrument (Gongyi City Yuhua Instrument Co., Ltd). ¹H NMR and ¹³C NMR spectra were recorded at 25 °C using a Bruker Avance 300 MHz spectrometer. Elemental analyses were performed on an Elementar Vario EL-III instrument. UV-Vis absorption spectra have been measured with Hitachi U-3500 recording spectrophotometer from quartz cuvettes of 1 cm path.

Steady-state emission and time-resolved decay curves were measured on an Edinburgh FLS 920 fluorophotometer equipped with time-correlated single-photon counting (TCSPC) card. With the aid of nF 900 soft ware, the prompt fluorescence lifetime (τ_F) was measured under detection of nF lamp at room temperature; while the phosphorescence lifetime (τ_P) and delayed fluorescence lifetime (τ_{DF}) were measured at room temperature and nitrogen atmosphere, under detection of microsecond xenon flash lamp (Edinburgh Analytical Instruments, μF 900). The monoexponential fit for prompt fluorescence decay and diexponential fits for phosphorescence and delayed fluorescence decays give acceptable statistics parameters of $\chi^2 < 1.1$. χ^2 is the “reduced chi-square”. Fluorescence quantum yields (Φ_f) were measured using quinine sulfate (in 0.1 mol·dm⁻³ aqueous NaOH, Φ_f = 0.53) as the standard according to literature.³⁸

Diode solid laser (532 nm, 60 mW·cm⁻²) was used as the excitation source for TTA upconversion that was observed with PR655 SpectraScan colorimeter. Upconversion efficiency (Φ_{UC}) was obtained relative to rhodamine 6G in ethanol according to Eq (1).²⁴

$$\Phi_{UC} = 2\Phi_r \left(\frac{A_r}{A_s} \right) \left(\frac{F_s}{F_r} \right) \left(\frac{\eta_s}{\eta_r} \right)^2 \quad (1)$$

Herein, the factor 2 accounts for the fact that two absorbed photons are required to produce one upconverted photon. Φ_r is the fluorescence quantum yield of rhodamine 6G as the reference standard (in ethanol, 0.5 μM , $\Phi_r = 0.88$).³⁹ A_s and A_r are the absorbency of sensitizer and rhodamine 6G under the excitation wavelength, respectively. F_s and F_r are the integrated emission of acceptor and rhodamine 6G under the excitation wavelength, respectively. n_s and n_r are the refractive index of solvent used in sample and reference measurements, respectively.

2.3 Upconversion-powered photoelectrochemistry

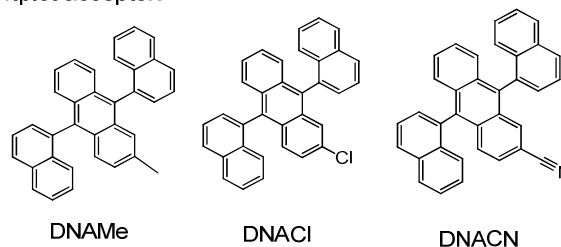
Upconversion-powered photoelectrochemistry^{40,41} was achieved in a three-electrode cell (electrolyte: 1.0 M H_2SO_4 in H_2O) with WO_3 film ($E_g = 2.7$ eV) deposited on ITO glass as working electrode, platinum rod as counter electrode and Ag/AgCl (0.1 M) as reference electrode. Firstly, diode-pumped solid-state laser (532 nm, 60 $\text{mW}\cdot\text{cm}^{-2}$) irradiates our upconverted o/w microemulsion to obtain green-to-blue upconversion. Then, the blue upconversion photo-activates the WO_3 working electrode and induce the photoelectrochemistry. The upconverted o/w microemulsion is filled inside a quartz cuvette of 1 cm path under air atmosphere, which is placed near the working electrode. Thus, the shuttered current/time response of the WO_3 photoanode biased to +0.33 V vs. Ag/AgCl was recorded by a computer controlled electrochemistry station.

Results and discussion

3.1 Absorption and emission

Very interested in enhancement TTA-UC efficiency (Φ_{UC}), we designed a series of new 9,10-dinaphthylanthracenes (Figure. 1), top-end-capped with naphthyl group on 9,10-position and flanked with different groups (such as $-\text{CH}_3$, $-\text{Cl}$ and $-\text{CN}$) on 2-position of the anthracene, whose names are abbreviated as DNAME, DNACl and DNACN, respectively. Triplet sensitizer Pd(II)tetratolylporphyrin, abbreviated as PdMeTPP, is also presented.

Triplet acceptor:



Triplet sensitizer:

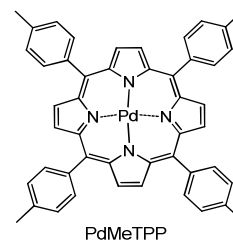


Figure 1 Molecular structures of 9,10-dinaphthylanthracenes (DNAME, DNACl and DNACN) and triplet sensitizer PdMeTPP.

9,10-Dinaphthylanthracenes show the characteristic vibronic absorption bands in the range of 350–450 nm and the emission spectra present the peaks at ~430 nm for DNAME and DNACl, while DNACN extends out to long wavelength at 452 nm due to its increasing molecular conjugation (Figure 2a). Calculated fluorescence quantum yields (Φ_f , %) are in order of DNAME (0.78) > DNACl (0.69) > DNACN (0.63), with concomitant of their fluorescence lifetime (τ_f , ns) increase from 3.81 ns (DNAME) to 3.98 ns (DNACl) till to 5.31 ns (DNACN) (see Table 1 and Figure 2b). These show that 9,10-dinaphthylanthracene with donating group (such as CH_3 -) on 2-position exhibits large radiation probability in comparison with those containing accepting group (such as $-\text{Cl}$ and $-\text{CN}$). We noticed that the absorption and emission spectra of 9,10-dinaphthylanthracenes in o/w microemulsion medium show similar to those in DMF solvent (see Figure 2a and Figure S2).

Table 1 Absorption and emission data of acceptors in DMF (1 μM)

Acceptor	λ_{ab} (nm)	λ_{em} (nm)	Φ_f (%)	τ_f (ns)
DNAME	362, 378, 399	431	0.78	3.81
DNACl	364, 381, 402	434	0.69	3.98
DNACN	353, 373, 396, 416	452	0.63	5.31

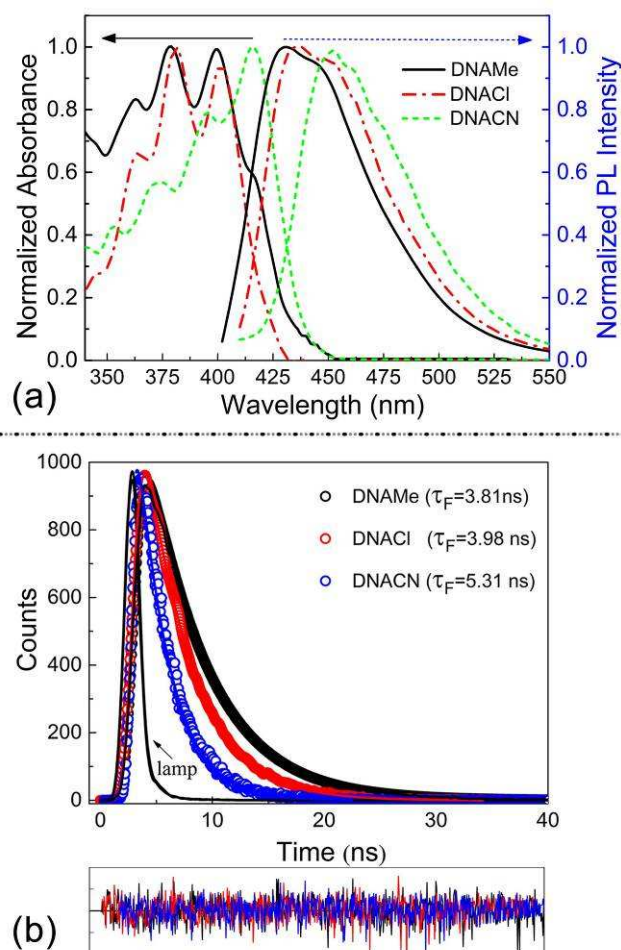


Figure 2 (a) Absorption and emission spectra of 9,10-dinaphthylanthracenes (in DMF, 1 μ M); (b) fluorescence time-resolved decay curves.

As shown in Table 2 and Figure 3, the absorption spectrum of sensitizer PdMeTPP in o/w microemulsion shows 2-nm red-shift in comparison with that in DMF. Meanwhile, the emission bands located at 569 and 611 nm with nanosecond lifetimes are confirmed to be fluorescence decays while the bands located at ~680 and ~750 nm with microsecond lifetimes to be phosphorescence decays.

Noted that both fluorescence and phosphorescence maxima of PdMeTPP are very similar in DMF and o/w microemulsion, but the particular decay times are quite different. Relative to those in DMF, the lifetimes of fluorescence and phosphorescence are decreased in the o/w microemulsion (Table 2), accompanying by dramatical decrease in fluorescence intensity (Figure 3). The reason for these observed differences in emission decay can be interpreted that the confined space and un-free collision between droplets in the o/w microemulsion could open the triplet state radiative relaxation pathway, which would have influence on triplet-triplet annihilated upconversion.

Table 2 Absorption and emission data of PdMeTPP in different mediums

medium	in DMF solvent	in o/w microemulsion
λ_{abs} , nm	418, 524	420, 526
λ_{fluor} , nm	569, 611	569, 611
λ_{phos} , nm	676, 750	680, 752
τ_F , ns	9.8 (13.87%), 19.1 (86.13%)	5.8 (17.63%), 19.5 (82.37%)
λ_{abs} , nm	418, 524	420, 526

τ_F and τ_P are fluorescence lifetime and phosphorescence lifetime, respectively.

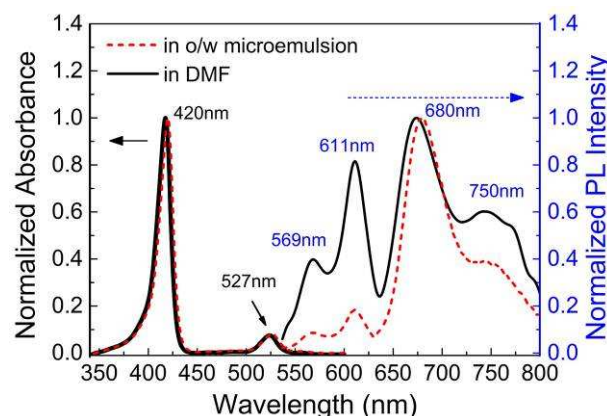


Figure 3 Absorption and emission spectra of PdMeTPP in DMF and o/w microemulsion (8 μ M, the emission spectra are obtained under the excitation of Q-band).

3.2 Structure/ TTA-UC performances in DMF

Under the excitation of diode laser (532 nm, 60 $\text{mW}\cdot\text{cm}^{-2}$), the green-to-blue upconversion from DNAMe was recorded (Figure 4), where the upconverted intensities exhibit almost quadratic integral enhancement (insert) as a function of incident power intensity at 10.89–55.97 $\text{mW}\cdot\text{cm}^{-2}$. These strongly suggest that the TTA-UC was a nonlinear optical process (As expressed in Eq. (1): two absorbed photons are required to produce one upconverted photon, that is quasi two-photon process).

Since two-photon process can occur in concentrated solution, the dependence of upconversion intensity on the concentration of 9,10-dinaphthylanthracenes (acceptor) is shown in Figure 5 (a–c). With the increasing of acceptor' concentration from 0.08 to 3.6 mM (doped with PdMeTPP at 8 μ M), the upconverted intensities of three 9,10-dinaphthylanthracenes are remarkably increased, showing 14.2-folds (DNAMe), 7.4-folds (DNACI) and 4-folds (DNACN) enhancements, respectively. Correspondingly, the efficiencies (Φ_{UC}) give the maximum values at 34.68% (DNAMe), 24.57% (DNACI) and 21.03% (DNACN), respectively (Figure 6), which is correlative with TTT efficiency (Φ_{TTT}) and TTA efficiency (Φ_{TTA}) as well as the acceptor' fluorescence quantum yield (Φ_f), that is, $\Phi_{\text{UC}} = \Phi_{\text{TTT}} \cdot \Phi_{\text{TTA}} \cdot \Phi_f^{42}$

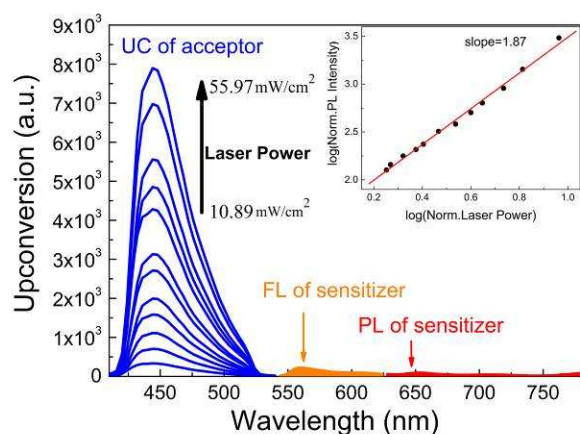


Figure 4 Upconverted intensity of DNAME following excitation of PdMeTPP (λ_{ex} =532 nm) measured as a function of incident power intensity (Inset: nearly double logarithm plot of the normalized upconverted emission of DNAME as a function of the normalized incident power intensity of the laser).

Triplet-triplet energy transfer (TTT) efficiency (Φ_{TTT}) can be evaluated according to Stern-Volmer equation (2), where P_o/P is the phosphorescence intensity of sensitizer without and with acceptor. τ_p and $[Q]$ are the phosphorescence lifetime of sensitizer and the concentration of acceptor, respectively. K_Q is the triplet quenching constant that can stand for the triplet-triplet energy transfer efficiency (Φ_{TTT}).

$$\frac{P_o}{P} = K_Q \tau_p [Q] + 1 \quad (2)$$

Thus, the relationship of P_o/P and $[Q]$ for 9,10-dinaphthylanthracenes were plotted (Figure 7) and the calculated triplet quenching constants (K_Q) are in the order of DNAME ($7.65 \times 10^8 \text{ M}^{-1} \cdot \text{s}^{-1}$) > DNACI ($3.89 \times 10^8 \text{ M}^{-1} \cdot \text{s}^{-1}$) > DNACN ($0.74 \times 10^8 \text{ M}^{-1} \cdot \text{s}^{-1}$), which approach the diffusion limit of the DMF solvent ($8.3 \times 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$ at 25 °C).⁴³ These indicate that TTT is a diffusion controlled process in the present experimental system. Based on the K_Q values, one can see that the TTT efficiency (Φ_{TTT}) are in the order of DNAME > DNACI > DNACN.

Delayed fluorescence decay curves of 9,10-dinaphthylanthracenes doped with PdMeTPP indicate that they have dual delayed fluorescence lifetimes (τ_{DF1} , τ_{DF2}) (Figure 8a and Table 3), which attributed to the dual phosphorescence of PdMeTPP (see Table 2). We noticed that the unconverted (residual) phosphorescence of PdMeTPP presents almost reduced phosphorescence lifetime (τ_{unp}) in the presence of acceptor (Figure 8b). Furthermore, for the sensitizer of PdMeTPP the unconverted (residual) phosphorescence lifetime increase is accompanied by the

decreased delayed fluorescence lifetime from DNACN (2.68, 13.37 μs), DNACI (2.28, 11.64 μs) to DNAME (0.93, 10.11 μs), which have positive contribution to triplet-triplet annihilated upconversion efficiency (see Table 3).

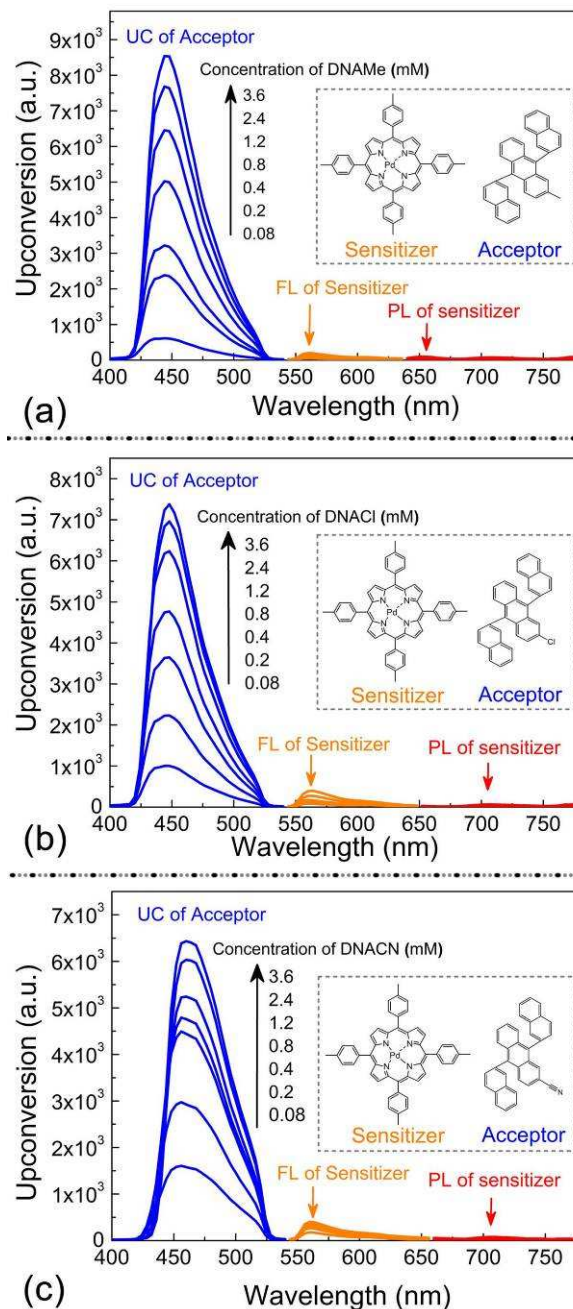


Figure 5 Dependence of upconversion intensity on concentration of (a) DNAME, (b) DNACI and (c) DNACN in degassed DMF, at fixed concentration of sensitizer (8 μM) under the excitation of 532 nm (60 $\text{mW} \cdot \text{cm}^{-2}$).

Based on the discussion of structure/TTA-UC performance correlations, it was found that 9,10-dinaphthylanthracene flanked with donating group (CH_3 -) on 2-position exhibit higher

fluorescence quantum yield (Φ_f) (see Table 1), larger triplet quenching constant (K_Q) and decreased delayed fluorescence lifetime (τ_{DF}), relative to those with accepting group (CN- and Cl-). As a result, the efficient upconversion efficiency (Φ_{UC}) was obtained as high as 34.68% in DMF.

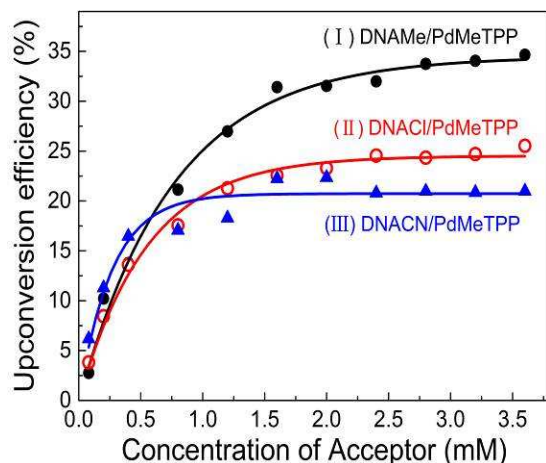


Figure 6 Dependence of upconversion efficiency on concentration of (a) DNAMe, (b) DNACl and (c) DNACN in degassed DMF, at fixed concentration of sensitizer (8 μ M) under the excitation of 532 nm (60 mW·cm⁻²).

Table 3 Upconversion properties of acceptors doped with PdMeTPP and unconverted phosphorescence lifetime of PdMeTPP in the presence of acceptors

Acceptor	λ_{UC} (nm)	Φ_{UC} (%)	K_Q (10 ⁸ M ⁻¹ s ⁻¹)	τ_{DF1}, τ_{DF2} (μ s)	τ_{unp} (μ s)
DNAMe	446	34.68	7.65	0.93 (1.45%) 10.11 (98.55%)	11.23 (52.55) 4.11 (47.45)
DNACl	448	24.57	3.89	2.28 (23.50%) 11.64 (76.50%)	10.48 (78.90) 0.80 (21.10)
DNACN	464	21.03	0.74	2.68 (17.36%) 13.37 (82.64%)	9.35 (72.07) 1.43 (27.93)

τ_{DF} is the lifetimes of delayed fluorescence of dinaphthylanthracenes and τ_{unp} is the unconverted phosphorescence lifetime of PdMeTPP.

3.3 TTA-UC performances in o/w microemulsion

TTA-upconversion performances in o/w microemulsion containing DNAMe and PdMeTPP are conducted without the need of deaerating anymore. These transparent upconverted o/w microemulsion are stable at the environment for several months and exhibit not only the concentration-dependent upconverted intensity that shows the similar to those in pure organic medium (Figure S3), but also the temperature-dependent upconverted intensity (Figure S4). It is interpreted³⁶ that the o/w (oil-in-water) microemulsion using nonionic surfactant as emulsifier can be reversibly converted

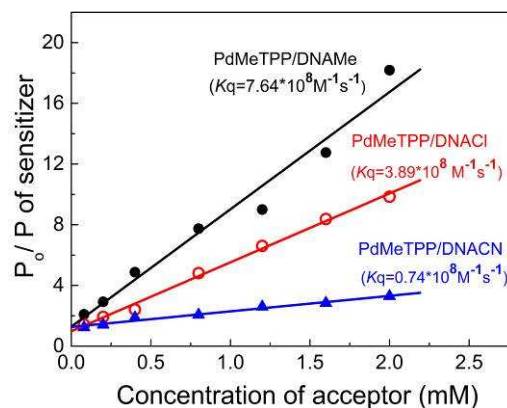


Figure 7 Stern-Volmer curves of PdMeTPP quenched by DNAMe (a), DNACl (b) and DNACN (c), upon excitation at 532 nm (60 mW·cm⁻²).

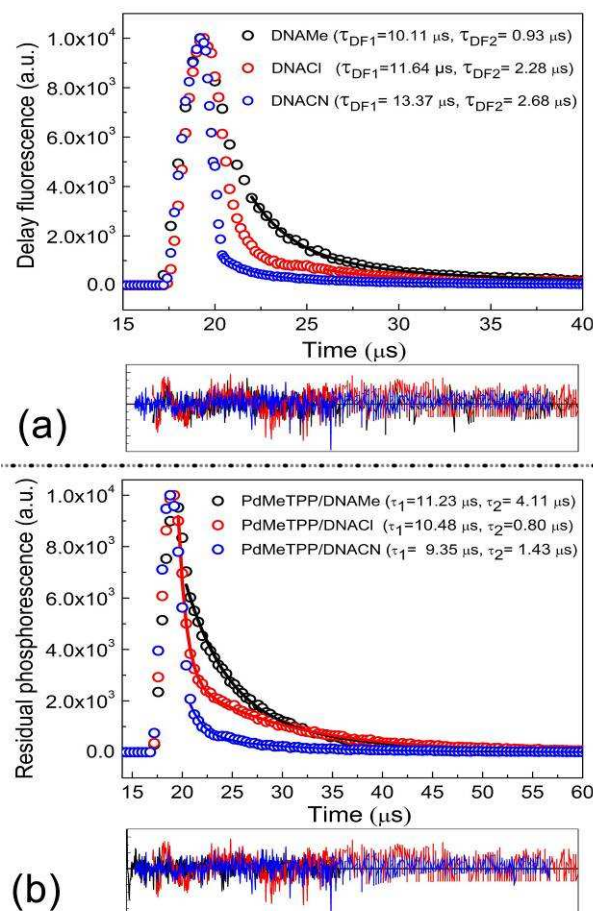


Figure 8 (a) Delay fluorescence curves of three 9,10-dinaphthylanthracenes doped with PdMeTPP, upon excitation at 532 nm and detection at $\sim$ 440 nm; (b) Unconverted phosphorescence decay curves of PdMeTPP in the presence of different 9,10-dinaphthylanthracenes, upon excitation at 532 nm and detection at $\sim$ 680 nm).

into w/o (water-in-oil) microemulsion with the phase inversion temperature (PIT). Below PIT the nonionic surfactant forming the microemulsion prefers a high curvature surface around oil; and

above the PIT the surfactant prefers a high curvature surface around water.³⁷ O/w microemulsion possesses the confined spaces that block the collision between sensitizers and acceptors, which is deleterious to upconversion performance. On the contrary, w/o microemulsion with oil continuous phase, the soluble sensitizer and acceptor are prone to diffusion and collision. Finally, not only TTT process but also TTA process are promoted, which make the Φ_{UC} value reach to the counterpart in pure organic solvent.

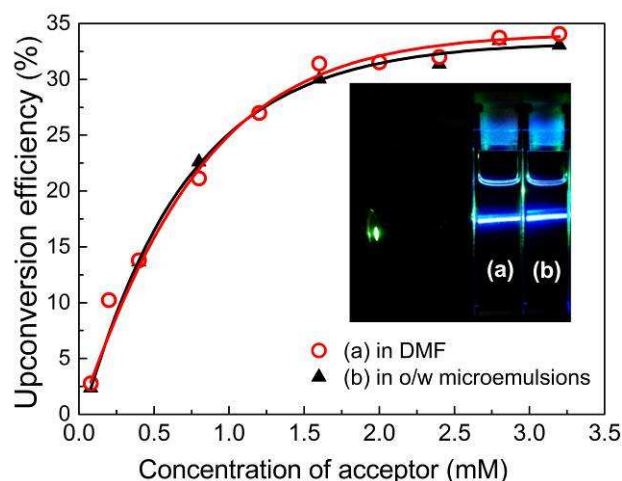


Figure 9 Concentration-dependent upconverted efficiencies of DNAME combined with PdMeTPP (fixed at 8 μM) in o/w microemulsion (70 $^{\circ}\text{C}$) and DMF (25 $^{\circ}\text{C}$), respectively. Insert is the photographs of blue upconversion from the systems above (The excitation source is diode laser at 532 nm and 60 $\text{mW}\cdot\text{cm}^{-2}$).

As shown in Figure 9, the enhanced upconversion efficiency (Φ_{UC}) in o/w microemulsion is almost the same as that in DMF (insert presenting the photographs of green-to-blue upconversion obtained from DNAME/PdMeTPP in o/w microemulsions and in DMF). Very importantly, this upconverted o/w microemulsion can keep high efficiency ($\Phi_{UC}=33.12\%$) without degassing for several days. Contrarily, the efficiency (Φ_{UC}) of counterpart in DMF decreases to naught within 1.2 hour without degassing (Figure 10). Moreover, a comparison experiment of DNAME/ PdMeTPP using o/w microemulsion, both with deaeration and without deaeration, has further confirmed that the upconverted o/w microemulsion is no need of deaerating anymore (Figure S5). These imply that the upconverted o/w microemulsion is not sensitive to the oxygen, which is of great significance. What's more, the temperature-dependent upconversion shows that the system with high upconverted efficiency (Φ_{UC}) is more sensitive to the temperature, which is probably used as the temperature sensor (Figure S6).

3.4 Upconversion-powered photoelectrochemistry

Upconverted o/w microemulsion can be employed as the desired light used in photoelectrochemistry. As shown in Figure 11a, the green-to-blue upconversion irradiates WO_3 film deposited on ITO that acts as the working electrode. Since WO_3 photoanode ($E_g = 2.7 \text{ eV}$, $\lambda_{ab} = 459 \text{ nm}$)⁴⁴ is able to absorb the blue illumination produced by our upconverted o/w microemulsion, the oxidation of water can take place on the WO_3 photoanode, meanwhile the hydrogen can be obtained at the platinum rod electrode. As a result, shuttered current/time response of a WO_3 photoanode biased to +0.33 V vs. Ag/AgCl was recorded by a computer controlled electrochemistry station.

Measurement data (Figure 11b) show that larger photocurrent ($I_f = 0.046 \mu\text{A}\cdot\text{cm}^{-2}$) was obtained under the irradiation by larger upconverted o/w microemulsion (DTAMe/PdMeTPP, $\Phi_{UC}=33.12\%$), while smaller photocurrent ($I_f=0.035\mu\text{A}\cdot\text{cm}^{-2}$) was recorded from small upconverted o/w microemulsion (DTACl/PdMeTPP, $\Phi_{UC} = 23.43\%$), strongly confirming that upconversion-driven photoelectrochemistry was indeed responsible for the generated photocurrent. In order to eliminate the photocurrent resulting from the excitation of diode pumped solid state laser, the contrastive experiments were conducted under the identical conditions excepting for using the quartz cuvette containing only blank solvent. Considering that the upconverted o/w microemulsion possesses absence of toxicity, easy to fabricate and unnecessary to deaerate, the o/w microemulsion can be a suitable medium for triplet-triplet annihilation upconversion.

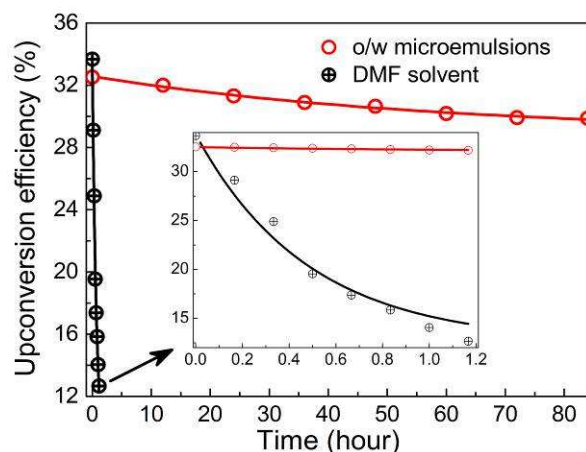


Figure 10 Time-dependent upconversion efficiency for DNAME/PdMeTPP (3.2 mM/8 μM) in o/w microemulsion (70 $^{\circ}\text{C}$) and DMF (25 $^{\circ}\text{C}$), respectively, under the air atmosphere. (The excitation source is diode laser at 532 nm and 60 $\text{mW}\cdot\text{cm}^{-2}$).

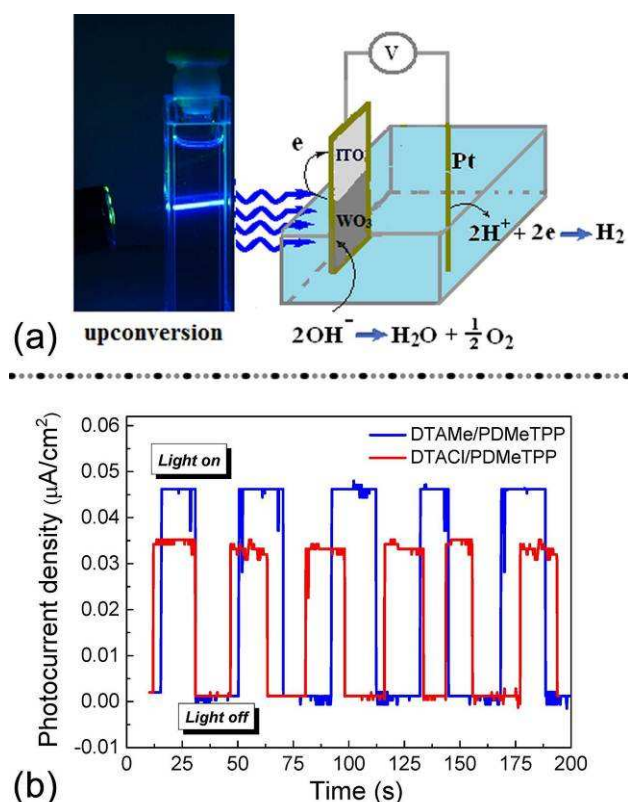


Figure 11 (a) Photograph of the upconversion-driven photoelectrochemical cell biased to +0.33 V vs. Ag/AgCl; (b) the corresponding recorded photocurrent curves illuminated by green-to-blue upconversion coming from the upconverted o/w microemulsions (70°C) under air atmosphere (The excitation source is diode laser at 532 nm and 60 mW·cm⁻²).

Conclusions

An effective medium for triplet-triplet annihilated upconversion was firstly reported and the correlations between structure/upconversion performance of three 9,10-dinaphthylanthracenes doped with sensitizer (PdMeTPP) were discussed. It was found that 9,10-dinaphthylanthracene (DNAME) with donating group exhibits high fluorescence quantum yield ($\Phi_F=78\%$) and larger TTT efficiency ($K_Q, 7.65 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$), in comparison with DNACl ($\Phi_F=69\%$, $K_Q=3.89 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$) and DNACN ($\Phi_F=63\%$, $K_Q=0.74 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$), resulting in the efficiency (Φ_{UC}) in the order of DNAME (34.68 %) > DNACl (24.57 %) > DNACN (21.03 %) in DMF solvent.

The fact of efficiency (Φ_{UC}) increase accompanied by the temperature increase for the upconverted o/w microemulsion can be interpreted that oil-in-water (o/w) containing nonionic emulsifier (Tween-20) can reversible converted to water-in-oil (w/o) microemulsion with the temperature changing, which would

promote the TTT and TTA processes with the result that the upconverted efficiency is enhanced. These demonstrated that thermal-driven upconversion mechanism is functioned. The maximum upconverted efficiency in o/w microemulsion was obtained as high as 33.12% that is comparable to the counterpart in DMF solvent (34.68%).

More importantly, it is no need for upconverted o/w microemulsion to deaerate any more, which is of critical importance for the application in photoelectrochemistry. The importance in this study suggests that the upconverted o/w microemulsion provides the simple approach to obtain high TTA-UC efficiency without degassing at all.

Acknowledgements

The authors are grateful to National Natural Science (Grant No.51273141, 51303122), Natural Science Foundation of Jiangsu Province (BK20130262), Natural Science Foundation of Jiangsu Provincial Department of Education (11KJA430003), the Opening Project (No. SJHG1311) of the Jiangsu Key Laboratory for Environment Functional Materials, Project of Person with Ability of Jiangsu Province (2010-xcl-015), Excellent Innovation Team in Science and Technology of Jiangsu Provincial Department of Education, and Project of Science and Technology of Suzhou (SYG201204) for financial supports.

Author Contributions

§These authors contributed equally to this work.

* The corresponding author.

Notes and references

^aJiangsu Key Laboratory for Environmental Functional Materials, School of Chemistry, Biology and Materials Engineering, Suzhou University of Science and Technology, Suzhou, 215009, P. R. China.

^bState Key Laboratory of Crystal Materials, Shandong University, Jinan, 250100, China.

†Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

1. G. S. He, P. P. Markowicz, T. C. Lin, P. N. Prasad, *Nature*, 2002, **415**, 767.
2. G. S. He, L. S. Tan, Q. D. Zheng, P. N. Prasad, *Chem. Rev.*, 2008, **108**, 1245.
3. X. M. Wang, D. Wang, G. Zhou, W. Yu, Y. Zhou, Q. Fang, M. H. Jiang, *J. Mater. Chem.*, 2001, **11**, 1600.
4. G. S. He, C. F. Zhao, J. D. Bhawalkar, P. N. Prasad, *Appl. Phys. Lett.*, **1995**, 67: 3703.
5. B. H. Cumpston, S. P. Ananthave, S. Barlow, D. L. Dyer, J. E. Ehrlich, L. L. Erskine, A. A. Heikal, S. M. Kuebler, I. S. Lee, D. M. Maughon, J. G. Qin,

- H. Rockel, M. Rumi, X. Wu, S. R. Marder, J. W. Perry, *Nature*, 1999, **398**, 51.
6. M. Zhang, M. Li, Q. Zhao, F. Y. Li, D. Q. Zhang, J. P. Zhang, T. Yi, C. H. Huang, *Tetrahedron Lett.*, 2007, **48**, 2329.
7. A. Karotki, M. Khurana, J. R. Lepock, B. C. Wilson, *Photochemistry and photobiology*, 2006, **82**, 443.
8. M. Albota, D. Beljonne, J. L. Bredas, J. E. Ehrlich, J. Y. Fu, A. A. Heikal, S. E. Hess, T. Kogej, M. D. Levin, S. R. Marder, D. McCord-Maughon, J. W. Perry, H. Rockel, M. Rumi, G. Subramaniam, W. W. Webb, X. L. Wu, C. Xu, *Science*, 1998, **281**, 1653.
9. S. Balushev, V. Yakutkin, T. Miteva, Y. Avlasevich, S. Chernov, S. Aleshchenkov, G. Nelles, A. Cheprakov, A. Yasuda, K. Mullen and G. Wegner, *Angew. Chem. Int. Ed.*, 2007, **46**, 7693.
10. M. T. Whited, P. I. Djurovich, S. T. Roberts, A. C. Durrell, C. W. Schlenker, S. E. Bradforth and M. E. Thompson, *J. Am. Chem. Soc.*, 2011, **133**, 88.
11. R. R. Islangulov, D. V. Kozlov, F. N. Castellano, *Chem. Commun.*, 2005, 3776
12. S. Balushev, V. Yakutkin, G. Wegner, T. Miteva, G. Nelles, A. Yasuda, S. Chernov, S. Aleshchenkov, A. Cheprakov, *Appl. Phys. Lett.*, 2007, **90**, 181103.
13. T. N. Singh-Rachford, A. Haefele, R. Ziessel and F. N. Castellano, *J. Am. Chem. Soc.*, 2008, **130**, 16164.
14. H. C. Chen, C. Y. Hung, K. H. Wang, H. L. Chen, W. S. Fann, F. C. Chien, P. Chen, T. J. Chow, C. P. Hsu and S. S. Sun, *Chem. Commun.*, 2009, **27**, 4064.
15. M. J. Michael, J. K. M. Mapel, T. D. Heidel, S. Goffri, M. A. Baldo, *Science*, 2008, **321**, 226.
16. S. Obregon, A. Kubacka, M. F. Garcia, G. Colon, *J. Catal.* 2013, **299**, 298.
17. T. Rantanen, M. L. Jarvenpaa, J. Vuojola, K. Kuninga, T. Soukka, *Angew. Chem*, 2008, 120, 3871.
18. T. Miteva, V. Yakutkin, G. Nelles and S. Balushev, *New J. Phys.*, 2008, **10**, 103002.
19. G. Y. Chen, J. W. Seo, C. H. Yang, P. N. Prasad, *Chem. Soc. Rev.*, 2013, 42, 8304.
20. T. Trupke, M. A. Green and P. Würfel, *J. Appl. Phys.*, 2002, **92**, 4117.
21. T. N. Singh-Rachford, A. Haefele, R. Ziessel, F. N. Castellano, *J. Am. Chem. Soc.*, 2008, **130**, 16164.
22. Y. C. Simon, S. Bai, M. K. Sing, H. Dietsch, M. Achermann, C. Weder, *Macromol. Rapid Commun.*, 2012, **33**, 498.
23. A. Monguzzi, M. Frigoli, C. Larpent, R. Tubino, F. Meinardi, *Adv. Funct. Mater.*, 2012, **22**, 13.
24. T. N. Singh-Rachford, F. N. Castellano, *Coord. Chem. Rev.*, 2010, **254**, 2560.
25. R. R. Islangulov, J. Lott, C. Weder and F. N. Castellano, *J. Am. Chem. Soc.*, 2007, **129**, 12652.
26. T. N. Singh-Rachford, F. N. Castellano, *J. Phys. Chem. A*, 2008, **112**, 3550.
27. J. H. Kim and J. H. Kim *J. Am. Chem. Soc.*, 2012, **134**, 17478.
28. J. H. Kim, F. Deng, F. N. Castellano, J. H. Kim, *ACS Photonics*, 2014, **1**, 382.
29. C. Wohnhaas, A. Turshatov, V. Mailander, S. Lorenz, S. Balushev, T. Miteva, K. Landfester, *Macromol. Biosci.* 2011, **11**, 772.
30. A. Monguzzi, M. Frigoli, C. Larpent, R. Tubino, F. Meinardi, *Adv. Funct. Mater.* 2012, **22**, 139.
31. Q. Liu, T. S. Yang, W. Feng, F. Y. Li, *J. Am. Chem. Soc.* 2012, **134**, 5390.
32. A. Turshatov, D. Busko, S. Balushev, T. Miteva, K. Landfester, *New J. Phys.*, 2011, **13**, 083035.
33. D. H. Chen, C. J. Chen, *J. Mater. Chem.*, 2002, **12**, 1557.
34. J. Tolia, M. Chakraborty, Z. V. P. Murthy, *Cryst. Res. Technol.*, 2012, **47**, 909.
35. Y. C. Simon, S. Bai, M. K. Sing, H. Dietsch, M. Achermann, C. Weder, *Macromol. Rapid Commun.*, 2012, **33**, 498.
36. F. Ostertag, J. Weiss, D. J. McClements, *J. Colloid Interface Sci.*, 2012, **388**, 95.
37. B. K. Paul, S. P. Moulik, *Current Science*, 2001, **80**, 990.
38. J. Olmsted, *J. Phys. Chem.*, 1979, **83**, 2581.
39. M. Fischer, *J. Georges, Chem. Phys. Lett.*, 1996, **260**, 115.
40. R. S. Khnayzer, J. Blumhoff, J. A. Harrington, A. Haefele, F. Deng, F. N. Castellano, *Chem. Commun.*, 2012, **48**, 209.
41. B. Wang, B. Sun, X. M. Wang, C. Q. Ye, P. Ding, Z. Q. Liang, Z. G. Chen, X. T. Tao, L. Z. Wu, *J. Phys. Chem. C*, 2014, **118**, 1417.
42. J. Z. Zhao, S. M. Ji, H. M. Guo, *RSC Adv.*, 2011, 1, 937.M.
43. Montalti, M.; Credi, A.; Prodi, A.; Gandolfi, M. T. *Handbook of Photochemistry*, 3rd ed.; CRC Press: Boca Raton, FL, 2005.
44. J. A. Seabold, K. S. Choi, *Chem. Mater.*, 2011, **23**, 1105.