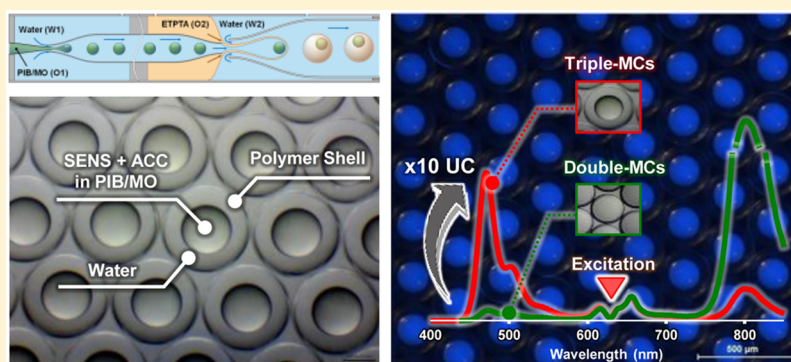


# Triple-Emulsion Microcapsules for Highly Efficient Multispectral Upconversion in the Aqueous Phase

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**ABSTRACT:** This study reports a new triplet-emulsion-based architecture for highly efficient triplet–triplet annihilation (TTA) upconversion (UC) in the aqueous phase. This encapsulation system separates the upconversion-emitting solvent core from the polymeric shell phase by utilizing an inner water phase. As a result, undesirable phosphorescence interference and chromophore loss were eliminated to achieve the aqueous upconversion efficiency close to those attainable in typical deoxygenated organic solvent systems. This system further allows various unconventional spectral shifting schemes, i.e., multicolor emission from monochromatic excitation (e.g., red to green and blue) or, conversely, frequency amplification of broad-band visible spectra to near-monochromatic shorter wavelength emission (e.g., green and red to blue), with minimal spectral impurities and interferences, representing a significant advance in encapsulated TTA-UC systems suitable for various aqueous-based applications.

**KEYWORDS:** anti-Stokes emission, energy conversion, microfluidics, microcapsule, upconversion

Upconversion (UC) refers to a process that achieves photon-frequency amplification or anti-Stokes shift via sequential absorption of two or more photons and subsequent emission of one higher energy photon. The UC represents a unique approach to enhance the efficiency of various solar-based technologies by enabling utilization of low-energy photons that are otherwise wasted and to develop unconventional imaging technologies. Among a few processes that achieve UC, triplet–triplet annihilation (TTA)-based UC has been receiving growing attention due to a few distinctively advantageous features such as (i) much higher upconversion quantum yield than any other UC processes reported to date, (ii) capability to upconvert a noncoherent light source at low irradiation power (e.g., solar irradiation), and (iii) no need for a high-temperature sintering step, which is required in lanthanide-based inorganic UC phosphor synthesis. TTA-UC is achieved through synchronous energy transfer between chromophores that fulfill specific energetic criteria, i.e., triplet–triplet energy transfer (TTET) between the sensitizer and acceptor as well as TTA between two excited acceptors.

Earlier attempts on TTA-UC exclusively employed organic solvents as a medium to dissolve organic and organometallic chromophores and contained them in an enclosed vessel after deoxygenation to prevent molecular oxygen quenching of excited sensitizers.<sup>1–3</sup> Recognizing the difficulty in applying such a design to real-world practices, oxygen-impermeable soft materials such as rubbery polymers have been considered as an alternate host.<sup>4–8</sup> However, restriction on chromophore mobility and reduced intermolecular energy transfer rate resulted in decreased quantum yield compared to the liquid phase UC. Gradual oxygen penetration has been another prevalent problem. Similar limitations exist for the particles, such as silica nanoparticles embedded with TTA-UC media.<sup>9,10</sup> An alternative approach of encapsulating TTA-chromophore-containing fluidic media within a micro- or nanoscale core–shell structure has been therefore considered more attractive.<sup>11–17</sup> A much higher quantum yield has been typically observed compared to other alternative host systems due to the

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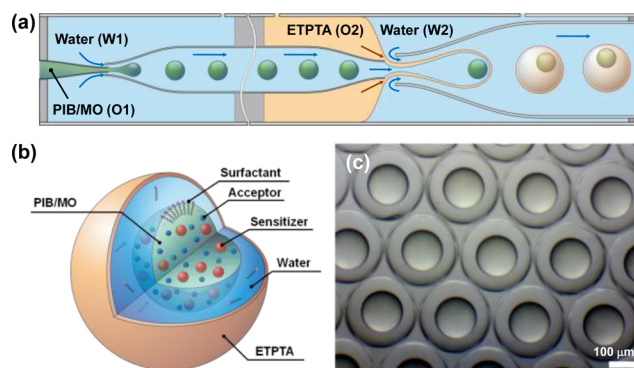
preservation of chromophore mobility in the fluidic core phase. In encapsulated systems, oxygen quenching has been commonly avoided by supplementing auxiliary components that chemically trap singlet oxygen.<sup>12,18</sup> The shell provides structural rigidity as well as partial oxygen blockage. These encapsulated systems can be applied in the form of a solid matrix for dry-phase applications and, more importantly, suspended in unconventional media such as water. Aqueous availability is of particular significance, prompting the translation of TTA-UC technology to aqueous-based applications such as photocatalysis, artificial photosynthesis, and bioimaging.

Although several different fabrication procedures have been explored,<sup>11–13,16–18</sup> all are in principal based on oil-in-oil-in-water (O/O/W) double emulsification followed by shell phase separation from the inner core. Herein, the first oil phase indicates a chromophore-containing solvent core, the second oil phase the rigid shell (e.g., cross-linked polymer), and the water phase the medium in which the core–shells are dispersed. One challenge that needs to be addressed is related to the inevitable loss of chromophores from the inner core due primarily to their facile diffusion to the shell before the complete phase separation. This results in the accumulation of chromophores inside the nonfluidic solid shell in which chromophore diffusion is severely limited and TTA-UC is consequently prohibited. This has been evidenced by strong sensitizer phosphorescence emission from core–shell TTA-UC systems reported in the past.<sup>11,12,14,18</sup> Since TTA-UC efficiency is significantly affected by the chromophores' concentration,<sup>19,20</sup> chromophore migration from the inner core to the shell also reduces the amount of chromophore available in the core where the TTA-UC functions, resulting in reduced overall UC efficiency.

In this study, we report a new core–shell architecture that prevents undesired phosphorescence emission based on an oil-in-water-in-oil-in-water (O1/W1/O2/W2) triple-emulsion configuration. The O1, W1, O2, and W2 phases denote the innermost core oil phase, core water phase, polymeric shell phase, and bulk water phase, respectively. The UC occurs in the innermost core oil phase that contains chromophore pairs, and the polymeric shell phase (second oil phase) provides a structural support, similarly to the past core–shell designs. The core water phase is herein newly introduced to play a distinctive role. It contains a surfactant that stabilizes the innermost oil phase and allows hosting of more than one innermost oil phase. More importantly, since chromophores are insoluble in water, it prohibits chromophore migration into the shell not only during the fabrication step but also during prolonged use. This new triple-emulsion microcapsule allows the TTA-UC with emission profile and efficiency that, for the first time, closely resemble those observed in bulk solvents due to elimination of undesirable phosphorescence interference and chromophore loss at the same time. The capability to host more than one core further allows multiple color emission and excitation within a single microcapsule, representing a significant advance in encapsulated TTA-UC systems.

## RESULTS AND DISCUSSION

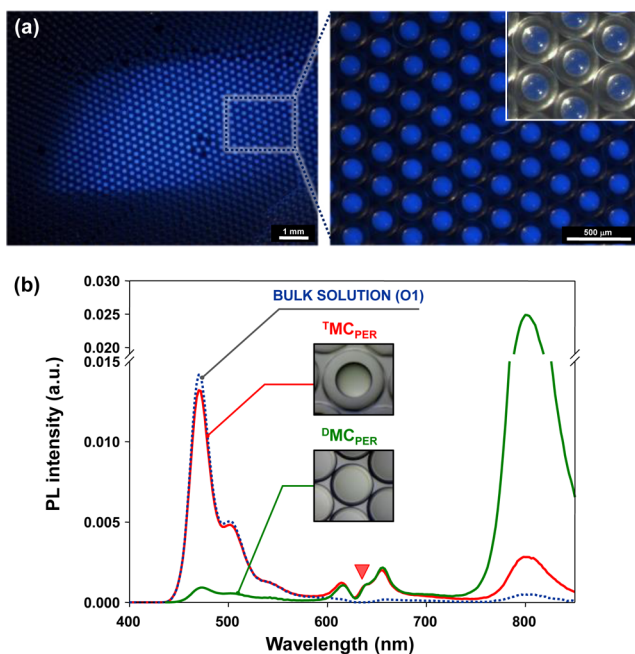
**Microfluidics Design.** A capillary microfluidic device (Figure 1a) was used to synthesize O1/W1/O2/W2 triple-emulsion microcapsules schematically drawn in Figure 1b. A couple of coaxially aligned glass capillaries first produced O1/W1 emulsion droplets. A polyisobutylene (4.0 wt %)/mineral oil solution (PIB/MO) containing a UC chromophore pair



**Figure 1.** Schematic illustration of the (a) microfluidic device and (b) single-core microcapsule prepared by the triple emulsion technique (<sup>T</sup>MC). (c) Optical microscope image of the prepared single-core <sup>T</sup>MC<sub>PER</sub>. Scale bar in (c) is 100 μm.

(O1) was injected through the leftmost injection capillary with a typical flow rate of 12 μL min<sup>-1</sup>. Here, the PIB/MO enables UC to occur without deoxygenation via singlet oxygen quenching as described in our previous study.<sup>12,18</sup> To enclose the O1 phase and form discrete droplets, the W1 phase containing Tween 20 (0.3 wt %) was introduced at a flow rate of 40 μL min<sup>-1</sup> through the first collection capillary, the end of which surrounds the injection capillary. The resulting O1/W1 droplets were further enclosed by the shell phase (O2), the ETPTA solution containing 1 wt % photoinitiator (Irgacure 2100), and 0.5 wt % Span 80. Resulting O1/W1/O2 emulsions were immediately dispersed in the W2 phase containing 1.5 wt % Pluronic F108. The O2 and W2 phases were sequentially injected through the interstice between the outlet of the first collection capillary and the inlet of the slightly wider second collection capillary at a flow rate of 13 and 120 μL min<sup>-1</sup>, respectively, but in opposite directions. The resulting suspension was then exposed to intense UV irradiation to instantaneously photocure the O2 phase and form a rigid outer shell. The microcapsules appeared exceptionally uniform, with a 260 and 160 μm capsule and core phase diameter, which was separated by a 40 μm thick water annulus. When placed on the surface, the microcapsules form a hexagonal packing due to structural uniformity, as shown in Figure 1c. They also form a stable suspension without any agglomeration even in the surfactant-free aqueous phase.

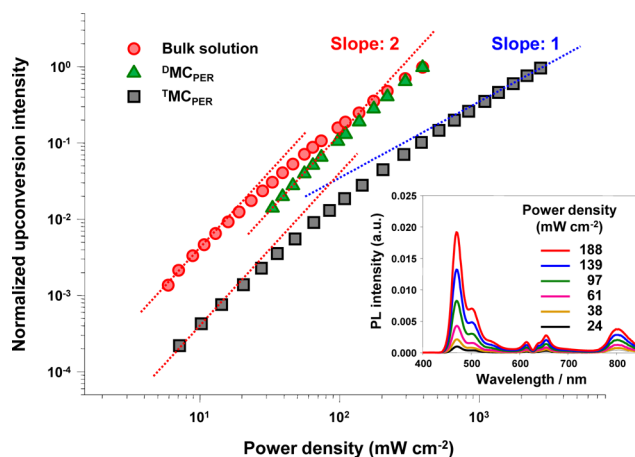
**Photoluminescence Properties of Triple-Emulsion UC Microcapsules.** The first set of microcapsules was synthesized using palladium tetraphenyltetrazaborporphyrin (PdTPBP) as a sensitizer and perylene (PER) as an acceptor to demonstrate red (~635 nm) to blue (~470 nm) upconversion in the triple-emulsion architecture. This pair has been often employed as a benchmark TTA-UC chromophore due to its commercial availability, photochemical stability, and relatively high UC quantum yield (~10%).<sup>7,21–23</sup> The steady-state absorption and Stokes emission spectra of PdTPBP/PER and other chromophores when dissolved in bulk PIB/MO are summarized in Figure S1. The triple-emulsion microcapsules with PER acceptor, denoted herein as <sup>T</sup>MC<sub>PER</sub>, emitted intense blue emission that was readily visible with the naked eye after a 600 nm short-pass filter under selective excitation at 635 nm, as shown in Figure 2a. The upconverted emission spectrum appeared almost identical to that of bulk PIB/MO under the same irradiation condition with the same chromophore composition, suggesting that the quantum yield of these



**Figure 2.** (a) Microscope images of the single-core  $^T\text{MC}_{\text{PER}}$  and (b) emission profiles of the single-core  $^T\text{MC}_{\text{PER}}$ ,  $^D\text{MC}_{\text{PER}}$ , and bulk O1 solution under monochromatic excitation at 635 nm. The peak indicated by a pink inverse triangle resulted from scattering of incident laser. Images were taken through a 600 nm short-pass optical filter. Inset in (a) is a microscope image of the single-core  $^T\text{MC}_{\text{PER}}$  under white light irradiation. Laser power:  $80 \text{ mW cm}^{-2}$ . Scale bar in (a) left: 1 mm, right:  $500 \mu\text{m}$ .

chromophore pairs in  $^T\text{MC}$  is similar to that in that bulk organic phase ( $\sim 6\%$ ). However, we were not able to accurately measure the absorbance and, as a result, the absolute quantum yield of suspended microcapsules, due to light scattering and reflection interferences. Regardless, these spectra epitomize the significant advancement from past core–shell structures such as a double-emulsion microcapsule ( $^D\text{MC}_{\text{PER}}$ ), which lacks the inner water separation layer. The emission spectrum of  $^D\text{MC}_{\text{PER}}$  suffers from significant sensitizer phosphorescence as well as much reduced upconversion emission as shown in Figure 2b. As a result, the overall emission from the  $^D\text{MC}_{\text{PER}}$  is the sum of the weak blue (upconverted emission from the core) and strong red (phosphorescence from the shell). In contrast,  $^T\text{MC}_{\text{PER}}$  produces almost pure blue, upconverted color, which was enhanced approximately 10 times compared to  $^D\text{MC}_{\text{PER}}$  in terms of the integrated upconversion emission area. Also note the intense light blue and green UC emission from single-core  $^T\text{MC}$ s made of different acceptors (9,10-bis(phenylethynyl)anthracene (BPEA) and a boron dipyrromethene derivative (BD2), with PdTPBP as sensitizer) shown in Figure S2.

The UC emission intensity of  $^T\text{MC}_{\text{PER}}$  was highly dependent on incident light power and showed apparent quadratic-to-pseudolinear dependency with a transient phase starting at approximately  $20 \text{ mW cm}^{-2}$ , as shown in Figure 3. The achievement of a linear dependency regime at lower light power irradiance is favorable for an efficient UC system, where most of the excited triplet acceptors are consumed by triplet fusion.<sup>24</sup> As expected, the power dependency of  $^T\text{MC}_{\text{PER}}$  appears to be closer to that of bulk O1 solution, whereas  $^D\text{MC}_{\text{PER}}$  shows a deviated tendency due to the reduced amount of available chromophores for the TTA-UC, which results in a “retarded”



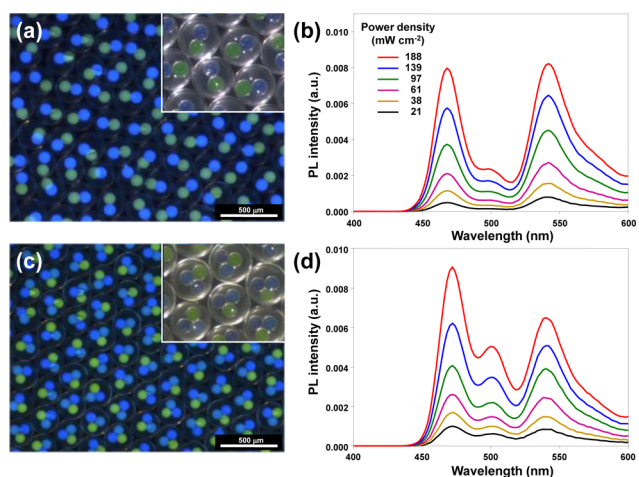
**Figure 3.** Normalized emission intensity of the  $^T\text{MC}_{\text{PER}}$ ,  $^D\text{MC}_{\text{PER}}$ , and bulk O1 solution at 470 nm as a function of the power density of the incident laser at 635 nm. The dashed lines in (b) present the linear fits with slopes of 1.0 (blue, linear) and 2.0 (red, quadratic), respectively. Inset shows emission profiles of  $^T\text{MC}_{\text{PER}}$  at different power densities. Note that the y-scale is normalized; the absolute upconversion efficiency is 9.6 times higher in  $^T\text{MC}_{\text{PER}}$  than in  $^D\text{MC}_{\text{PER}}$ .

quadratic dependency up to  $\sim 90 \text{ mW cm}^{-2}$ . The prepared  $^T\text{MC}_{\text{PER}}$  exhibited remarkable photostability under continuous laser irradiance at low power as shown in Figure S3, yet a slight photobleaching was observed at higher laser power density ( $97 \text{ mW cm}^{-2}$ ). In addition, as the incident laser power was increased, the lag time between laser irradiance and actual UC emission was decreased. As discussed in our previous paper, this might be due to the faster local depletion of oxygen by chemical quenching with PIB at higher laser power.<sup>18</sup>

**Multispectral Emission of UC Microcapsules.** The newly developed triple-emulsion architecture further allows more than one UC system to independently function within a single microscale containment for various spectral shifting scenarios. This is achieved by injecting more than one O1 phase containing different chromophore pairs into the W1 phase such that more than one UC system is encapsulated within one microcapsule. The surfactant presented in the inner water phase (Tween 20) stabilizes the innermost oil drops and prevents coalescence. As the first example, multicolor UC emitting microcapsules were fabricated by encapsulating two or three O1 phases, each containing different acceptors but the same sensitizer. The  $^T\text{MC}$  that encapsulated double cores (PdTPBP/PER and PdTPBP/BD2, denoted as  $^T\text{MC}_2$ ) exhibited distinctive blue (470 nm) and green (540 nm) UC emissions under monochromatic excitation at 635 nm that can be seen by the naked eye (Figure 4a). The emission spectrum was the sum of two independent emissions by PER and BD2 with minimal overlap (Figure 4b). By injecting additional oil core containing PdTPBP/BPEA,  $^T\text{MC}$ s with triple cores were obtained (Figure 4c, denoted as  $^T\text{MC}_3$ ). This microcapsule exhibited three distinctive emission peaks (Figure 4d). The perylene UC emission centered around 470 nm became stronger due to the spectral overlap with BPEA emission. However, BPEA UC emission centered around 500 nm did not increase as much as perylene emission presumably due to trivial absorption by neighboring BD2. Also see the low-magnification microscope image of  $^T\text{MC}_2$  and  $^T\text{MC}_3$  in Figure S4.

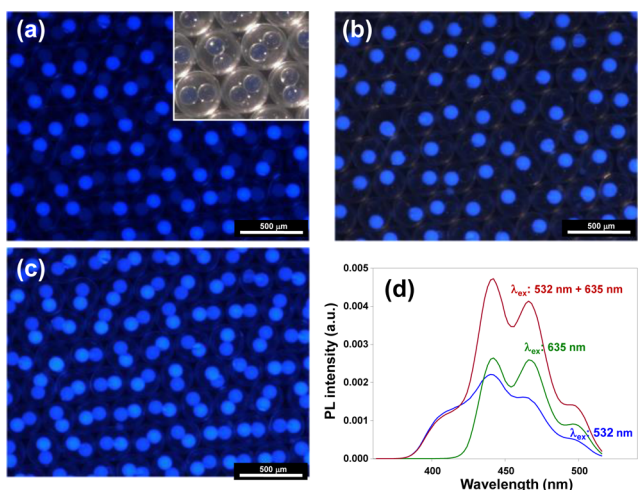
**Multispectral Absorption of UC Microcapsules.** Encapsulating individual O1 droplets having different sensi-





**Figure 4.** Microscope images and emission profile of (a, b)  $TMC_2$  and (c, d)  $TMC_3$  under monochromatic excitation at 635 nm. Images were taken through a 600 nm short-pass optical filter. Laser power: 80  $mW\ cm^{-2}$ . Scale bar in (a), (c): 500  $\mu m$ .

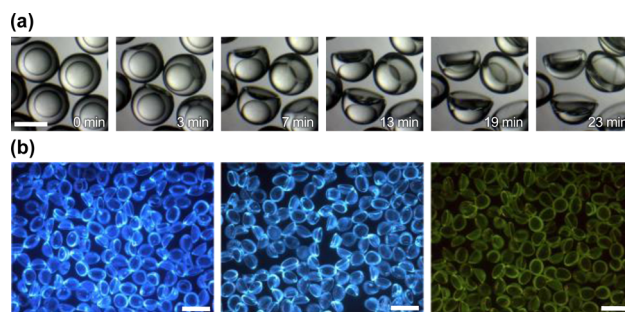
tizers enables multicolor upconversion to a common higher wavelength target. We synthesized dual-core  $TMC$  with individual O1 phases of PdTPBP/PER and platinum octaethylporphyrin (PtOEP)/9,10-diphenylanthracene (DPA) pairs, which achieved upconversion to blue from simultaneous dichromatic laser excitation with green (532 nm) and red (635 nm), denoted as  $TMC_4$ . PtOEP/DPA was used herein since this pair has been frequently employed to achieve green-to-blue TTA-UC,<sup>8,10,12</sup> while perylene can also be employed as an acceptor to produce green-to-blue TTA-UC in conjunction with PtOEP. We chose DPA, as it has a larger anti-Stokes shift and thus can produce upconverted photons with higher energy than perylene. Under each monochromatic excitation at 532 or 635 nm, only one of two cores selectively emitted UC fluorescence depending on the sensitizer, as shown in Figure 5a,b, while both cores were activated under simultaneous



**Figure 5.** Microscope images of  $TMC_4$  under monochromatic excitation at (a) 532 nm, (b) 635 nm, and (c) simultaneous dichromatic excitation at 532 and 635 nm. (d) Emission profiles of  $TMC_4$  under each excitation. Images were taken at the identical spot through a 500 nm short-pass optical filter. Laser power at 532 nm: 40  $mW\ cm^{-2}$ ; laser power at 635 nm: 80  $mW\ cm^{-2}$ . Scale bar in (a)–(c): 500  $\mu m$ .

dichromatic excitation (Figure 5c). The emission intensity profile of  $TMC_4$  under the dichromatic excitation was almost identical to the numerical summation of two profiles obtained from each monochromatic excitation, implying independent UC emission from two different cores (Figure 5d). There are only a few reports that attempted TTA-UC with two sensitizers and a single acceptor for broader wavelength absorption and a single UC emission in a homogenized solution,<sup>25</sup> but this study is the first instance of compartmentalizing independent UC systems on the microscale. When the two UC systems (PtOEP/DPA and PdTPBP/PER) are simply mixed in a homogeneous manner, TTET from  $^3PtOEP^*$  to  $^1perylene^0$  rather than  $^1DPA^0$  prevails such that DPA's characteristic fluorescence in the 390 to 430 nm range would be diminished (Figure S5). Such a detrimental interference can be avoided by physically segregating the PtOEP/DPA system from the PdTPBP/PER system in the double core of  $TMC$ , while the whole system still achieves the beneficial broad band absorption and additive upconversion emission.

**Deformation of UC Microcapsules under Mild Heating Conditions.** The  $TMCs$  maintained physical structure with the loss of UC emission less than 10% over a long period of time (>2 month) when stored in surfactant-free water. However, when dried under mild heating conditions (60 °C), the microcapsule ruptured and the inner water phases were released due to the evaporation of the inner water phase, as shown in Figure 6a, resulting in a contact lens-like shape.



**Figure 6.** (a) Microscope images of the  $TMC_{PER}$  as a function of exposure time at 60 °C. (b) Microscopic images of the ruptured  $TMCs$  that contain PdTPBP/PER, PdTPBP/BPEA, and PdTPBP/BD2 (left to right) under irradiation at 635 nm. Images were taken through a 600 nm short-pass optical filter. Scale bar in (a): 200  $\mu m$ , (b): 500  $\mu m$ .

However, even after complete drying, we found that the ruptured  $TMCs$  still emitted intense UC (Figure 6b), indicating that the UC media still remained inside the squeezed polymer shell. We believe that this heat-triggered eruption of the UC microcapsule might be useful in some applications, for example, simultaneous UC-mediated visualization and site-specific water-soluble drug delivery, while actual demonstration is out of the scope of this study and requires further research.

## CONCLUSIONS

This study presents the first successful synthesis of a highly unique aqueous-stable, microscale-encapsulated TTA-UC system that eliminates undesired sensitizer phosphorescence and achieves UC efficiency as high as those reported with a deoxygenated organic solvent host. The  $TMC$  allows various spectral shifting schemes, i.e., multicolor emission from monochromatic excitation or, vice versa, multicolor absorption

to monochromatic emission, with minimal spectral impurities and interferences.

## ■ EXPERIMENTAL METHODS

**Materials.** PdTPBP and PtOEP were purchased from Frontier Scientific. Perylene, BPEA, and DPA were purchased from Aldrich. BD2 was synthesized as in the literature.<sup>19</sup> The sensitizer/acceptor stock solutions were prepared by dissolving an appropriate amount of chemicals in tetrahydrofuran (THF). A certain volume of chromophore stock solutions was then added to a PIB (Polyscience)/MO (Aldrich) solution (4.0 wt %). The solution was placed in a convection oven at 70 °C for more than 12 h to evaporate THF, cooled, and kept in the dark at room temperature for further use as the innermost phase of the triple emulsion. The typical concentration of PdTPBP and perylene in PIB/MO is 3  $\mu\text{M}$  and 0.96 mM, respectively. A 0.3 wt % aqueous solution of polysorbate (Tween 20, Aldrich) and a 1.5 wt % aqueous solution of ethylene oxide–propylene oxide–ethylene oxide triblock copolymer (Pluronic F108, BASF) were used as the secondary continuous phase to generate a PIB/MO droplet and the primary continuous phase of the triple emulsion, respectively. An ethoxylated trimethylpropanetriacylate ester (ETPTA, SR 454, Sartomer) solution, the photocurable outermost oil phase of the triple emulsion, was prepared by adding photoinitiator (1 wt %, Irgacure 2100, BASF) and surfactant (0.5 wt %, Span 80, Aldrich) to ETPTA.

**Microfluidic Device.** The microfluidic device was prepared by coaxially arraying three different cylindrical glass capillaries in two square capillaries (1.05 mm i.d., #8100-100, Vitrocom) as illustrated schematically in Figure 1a. The primary injection and collection round capillaries (0.58 mm i.d.  $\times$  1.0 mm o.d., #B100-58-100, Friedrich & Dimmock) were tapered with a micropipette puller (P-97, Sutter instrument), whereas the middle capillary was prepared by heating and hand-pulling a commercial glass capillary (0.2 mm i.d.  $\times$  0.33 o.d., #CV2033, Vitrocom). To generate multiple core droplets, a four-barrel capillary (4B100-50-100, Friedrich & Dimmock) was used as the primary injection capillary instead of a single-barreled one. The left side of the primary collection and middle capillaries was treated with 2-[methoxy(polyethyleneoxy)propyl]-trimethoxysilane (Tech90, Gelest) in toluene, whereas the outer surface of the middle capillary was treated with trimethoxy(octadecyl)silane (Aldrich) prior to junction to render the surface hydrophilic or hydrophobic, respectively. The typical diameters of each capillary are depicted in Figure S8. The flow rates were individually controlled using syringe pumps (Harvard Apparatus). The typical flow rate of O1, W1, O2, and W2 used to make single-core <sup>T</sup>MC was 12, 40, 13, and 120  $\mu\text{L min}^{-1}$ , respectively. The generated triple-emulsion drops were rapidly cured by UV illumination using two black lamp bulbs (4 W), collected, and washed with and stored in deionized water.

**Spectroscopic and Microscopic Measurements.** The steady-state absorption spectra and Stokes emission spectra of the chromophore solution were analyzed on a UV–visible spectrophotometer (Agilent 8453) and spectrofluorometer (Shimadzu, RF-5301), respectively. Stokes and anti-Stokes emission spectra of the UC solutions and MCs were obtained with commercial diode lasers (532 and 635 nm) as the excitation sources. Emission from the solution in a cuvette was collected normal to the excitation and passed through a series of focusing lenses and an optical chopper (120 Hz) before

reaching a monochromator (Oriel Cornerstone, Newport Corp.). For the measurement of emission from the MCs, the laser beam was irradiated to a cuvette containing precipitated MCs in water at an approximately 40° angle. To remove any scattered light from the laser, a 632.8 nm notch filter, a 500 nm short-pass filter, or a 600 nm short-pass filter was mounted in front of the detector depending on the excitation sources. The signal was detected by an Oriel photomultiplier tube and processed by an Oriel Merlin radiometry detection system (Newport Corp.). Incident laser power was adjusted through the use of a round-type neutral density filter and was measured using a Nova II power meter/photodiode detector head (Ophir). The microscopic images were taken by a stereomicroscope (Leica, DMS300) coupled with the optical short-pass filters.

## ■ ASSOCIATED CONTENT

### Supporting Information

Molecular structure, normalized absorption and emission spectra of sensitizers and acceptors, UC emission intensity of <sup>T</sup>MC<sub>PER</sub> as a function of the laser exposure time, low-magnification microscope images of <sup>T</sup>MCs, dimensions of the capillary glasses. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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