Bifunctional Platinated Nanoparticles for Photoinduced Tumor Ablation

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Photoinduced nanomedicine is of particular interest as an emerging paradigm toward precise cancer therapy, as evidenced by the recent developments of nanoparticles such as polymeric micelles, vesicles, and inorganic nanomaterials for photoinduced therapy such as photodynamic therapy (PDT) and photothermal therapy (PTT). These nanoparticles that allow photosensitizers (PS) to effectively generate singlet oxygen ($\text{O}_2^*$) from tissue oxygen under light irradiation, have shown great capacity to selectively damage cancer cells for enhanced therapeutic efficiency, owing to their good resistance to photo-bleaching, preferable tumor accumulation, as well as effective intracellular translocation of PS. However, the exploration of the nanoparticles is still encounter some major limitations including impaired singlet oxygen quantum yield within nanoparticles, severe local hypoxia from depletion of tissue oxygen, as well as frequently encountered residual tumor cells surviving from PDT treatment, thereby resulting in unsatisfactory photoinduced anticancer efficiency. Although the integration of PS and other anticancer agents such as photothermal agent and chemotherapeutic compound within nanoparticles can facilitate their therapeutic efficacy. Consequently, it is highly desired to explore a novel paradigm of highly efficient nanoparticles that can achieve photoinduced cancer therapy of PS with tumor ablation.

Recently, some essential fluorophore cores such as boron dipyrromethene (BDP), porphyrin, and phthalocyanine, have been extensively explored to synthesize highly efficient PS with reduced radiative transition through their chemical modifications owing to their tunable photo-physical characteristics and structure flexibility. For instance, BDP as a versatile and robust fluorophore core can be activated as PS with enhanced singlet oxygen quantum yield through the halogenation-mediated heavy atom effect, spin converter (e.g., $C_{60}$), charge recombination, and orthogonal dye dimerization, which can promote the intersystem crossing of PS from singlet state ($S_1$) to triplet state ($T_1$) upon light irradiation and subsequent singlet oxygen generation. However, most of fluorophore cores can still display remarkable radiative transition that can generally lead to the generation of fluorescence, thereby impairing their singlet-to-triplet transition and nonradiative decay. Although various nanoparticles have been explored to improving their generation of singlet oxygen and subsequent accessibility to target organelles such as nucleus and mitochondria for improving their PDT efficiency, there are still significant absence of available nanoparticles that can induce the ultralow radiative transition of fluorophore cores such as BDP for maximizing their photoinduced anticancer efficacy.

Platinum (Pt) as a noble metal element has attracted considerable interests in the field of nanomedicine including cancer therapy, bioimaging, and bioanalysis. For instance, Pt can be utilized to synthesize Pt-based complexes or nanoparticles for cancer therapy or imaging owing to its superior biological functions. Unfortunately, Pt has been explored with limited success in the fabrication of platinated nanoparticles with ultralow radiative transition of fluorophore cores for in vivo photoinduced tumor ablation. Interestingly, Pt as a heavy atom possesses the high spin–orbit coupling constant ($\chi = 4481 \text{ cm}^{-1}$) that can promote the rapid intersystem crossing of singlet-to-triplet with a high rate of $10^{12} \text{ s}^{-1}$ and simultaneously has the unoccupied $d_{x^2-y^2}$ orbitals of square planar Pt(II) that may provide nonradiative decay from excited state to ground state through the $d-d$ energy band transition. Hence, the rational design of platinated nanoparticles might play a key role for facilitating ultralow radiative transition of fluorophore cores in photoinduced therapy, potentially resulting in singlet-to-triplet transition and nonradiative decay. Here, we report the bifunctional self-assembled nanoparticles of platinated BDP core (Bodiplatin-NPs) with ultralow radiative...
transition for photoinduced cancer therapy with tumor ablation (Scheme 1). Bodiplatin-NPs can produce both remarkable singlet oxygen and photothermal effect through their preferable singlet-to-triplet transition and nonradiative decay under single-wave light irradiation, thereby generating abundant reactive oxygen species (ROS) and potent hyperthermia at tumors. Moreover, Bodiplatin-NPs exhibit enhanced resistance to photobleaching, negligible dark toxicity, effective intracellular translocation from the lysosomes to cytoplasma, and preferable tumor accumulation, facilitating remarkable photoinduced cell damage and subsequent synergy between PDT and PTT for tumor ablation.

Bodiplatin-NPs were fabricated through the multiple synthetic procedures (Figure 1A and Figure S1, Supporting Information). Briefly, meso-pyridyl boron dipyrromethene-dsyl (BDP-phenOH) was first synthesized through the double Knoevenagel condensation of meso-pyridyl boron dipyrromethene with 4-hydroxyl benzaldehyde. Then, BDP-phenOH was used to synthesize Bodipy and meso-pyridyl boron dipyrromethene propyne (BDP-propyne) using tetraethylene glycol and propynyl group, which were further platinated to afford Bodiplatin and Bodiplatin-propyne, respectively (Figure S1, Supporting Information). Finally, Bodiplatin-propyne was conjugated with polyoxyethylene azide (MW 5000) through the Cu(I)-mediated click chemistry for synthesizing PEGylated Bodiplatin, which was then self-assembled into the micellar Bodiplatin-NPs with critical micelle concentration (CMC) of 0.9 μg mL⁻¹ (data not shown) in aqueous solution through film dispersion method (Scheme 1A). Additionally, Bodipy was utilized as a control with fluorescent core (Figure 1A). The chemical structures and compositions were fully characterized using ¹H NMR, ¹⁹F NMR, and ESI-MS analysis (Figure S2–S4, Supporting Information).

To characterize self-assembled Bodiplatin-NPs, transmission electron microscopy (TEM) was first used to observe their morphology. Bodiplatin-NPs exhibited a spherical morphology with 42.0 ± 6.0 nm diameter in aqueous solution (Figure 1B). Dynamic light scattering (DLS) shows that Bodiplatin-NPs had an average hydrodynamic size of 72.0 nm (Figure 1C), suggesting that these nanoparticles might be able to generate potential targeting capability via enhanced permeability and retention (EPR) effect. X-ray photoelectron spectroscopy (XPS) pattern further indicates that Bodiplatin-NPs exhibited the peaks at 72.5 and 75.8 eV, suggesting the presence of Pt(4f) in the nanoparticles (Figure 1D). Moreover, the energy dispersive X-ray spectroscopy (EDX) analysis further exhibited the characteristic F and Cl peaks at 0.5 and 2.6 eV (Figure 1E), respectively, indicating the presence of F from BDP core and Cl from platinated moiety within the hydrophobic cores of micellar nanoparticles as well.

As shown in Figure 2A, both Bodiplatin-NPs and Bodiplatin in aqueous solutions displayed the absorption peaks of about 680 nm in near-infrared (NIR) region, and these peaks were
red-shifted and broadened as compared to that of Bodiplatin in DMF solution. Possibly, the formation of J-type aggregates with π-π stacking within the micellar cores accounts for their broad red-shifted absorbances,[11] which is highly advantageous to achieve deep light penetration in tissue. Obviously, Bodiplatin-NPs have a suitable absorbance in NIR region for photoinduced cancer therapy. Subsequently, the size stability of Bodiplatin-NPs was evaluated in aqueous solutions. It shows that Bodiplatin-NPs exhibited a negligible size change during 7 d, implying that Bodiplatin-NPs are capable of maintaining a stable micellar nanostructure in aqueous solution (Figure S5, Supporting Information). In addition, Bodiplatin-NPs also exhibited a good chemical stability in culture medium (Figure S6, Supporting Information). Reasonably, the strong π-π interaction between BDP cores within micellar hydrophobic cores might account for their good stability.[12] Moreover, the resistance of Bodiplatin-NPs to photobleaching was also evaluated since it plays an important role for photoinduced therapy (Figure 2B). Bodiplatin-NPs exhibited much slower decrease in the absorbance under NIR light irradiation during 15 min as compared to Bodiplatin. Remarkably, the self-assembled nanostructure can protect the unsaturated bonds of BDP core from the damage of radicals in solution.[13] Therefore, Bodiplatin-NPs can provide more efficient treatment upon light irradiation as compared to Bodiplatin owing to their enhanced resistance to photobleaching.

To explore the potential photoconversion behavior of Bodiplatin-NPs under light irradiation, we firstly evaluated their capacity to produce singlet oxygen using 1,3-diphenyliso-benzofuran (DPBF) as a singlet oxygen probe.[14] Figure 2C shows that both Bodiplatin-NPs and Bodiplatin produced abundant singlet oxygen under 5 min irradiation (660 nm, 0.5 W cm⁻²), and also exhibited concentration-dependent generation of singlet oxygen (Figure S7, Supporting Information),[13] while Bodipy as a fluorophore core exhibited a negligible ability to produce singlet oxygen. Obviously, Bodiplatin-NPs exhibit a preferable ability to generate singlet oxygen as compared to Bodiplatin, probably owing to their enhanced photostability and reduced singlet oxygen self-quenching in self-assembled nanostructure. Subsequently, their singlet oxygen quantum yields ($\Phi_\Delta$) were further evaluated (Figure S8, Supporting Information). Bodipy as a control only had a negligible singlet oxygen quantum yield ($\Phi_\Delta = 0.02$) owing to its remarkable radiative transition.[5c,8] However, Bodiplatin-NPs and Bodiplatin exhibited the $\Phi_\Delta$ values of 0.34 and 0.28 in aqueous solutions, respectively, which are more preferable as compared to that of
Figure 2. A) Absorbance spectra of Bodiplatin-NPs and Bodiplatin in various solvents. B) Normalized absorbance of Bodiplatin-NPs and Bodiplatin in aqueous solutions at different time under irradiation (660 nm, 0.5 W cm$^{-2}$). C) Normalized absorbance of DPBF at 410 nm in the presence of Bodiplatin-NPs, Bodiplatin, and Bodipy at the concentration of 0.75 × 10$^{-6}$ M under irradiation (660 nm, 0.5 W cm$^{-2}$). D) Phosphorescence lifetime of Bodiplatin-NPs, Bodiplatin, and Bodipy at the concentration of 10.0 × 10$^{-6}$ M under irradiation. E) Phosphorescence spectra of Bodiplatin-NPs, Bodiplatin, and Bodipy at 77 K. F) Nanosecond transient absorption spectra of Bodiplatin at various excitation time. G) Temperature elevation of Bodiplatin-NPs, Bodiplatin, and Bodipy at the concentration of 30 × 10$^{-6}$ M under irradiation (660 nm, 0.5 W cm$^{-2}$). H) Fluorescence lifetime of Bodiplatin-NPs, Bodiplatin, and Bodipy at the concentration of 10.0 × 10$^{-6}$ M using fluorescence lifetime spectrometer.
widely used PS, free Ce6 (ΦΔ = 0.22) (Figure S9, Supporting Information). Distinctly, the platination of BDP core causes the effective generation of singlet oxygen. Moreover, Bodiplatin-NPs and Bodiplatin exhibited the enhanced phosphorescence lifetime of 2.0 and 1.3 ns as compared to Bodipy (0.2 ns), respectively (Figure 2D). Subsequently, the phosphorescence spectra of Bodiplatin-NPs were observed at 77 K. Bodiplatin-NPs and Bodiplatin exhibited the enhanced phosphorescence intensities when compared with Bodipy (Figure 2E), suggesting a favorable singlet-to-triplet transition for platinated BDP under irradiation. We also investigated the emission spectra of Bodipy and Bodiplatin in the presence or absence of oxygen at 295 K. Remarkably, the emission intensity of Bodiplatin was distinctly quenched by oxygen (Figure S10, Supporting Information), thereby confirming the presence of phosphorescence in their emission of platinated BDP. In addition, the nanosecond time-resolved transient difference absorption spectroscopy measurements show that Bodiplatin-NPs had the triplet excited state lifetime of 2.51 μs with relatively high triplet excited state quantum yield (Φτ = 0.6) (Figure S11, Supporting Information), while Bodipy had no detectable triplet excited state lifetime and quantum yield. It confirms that the platinated nanoparticles possess more accessible triplet excited state as compared to Bodipy, and have preferable capacity to achieve singlet-to-triplet transition for singlet oxygen generation. As a result, the platination of BDP core plays a key role in the generation of singlet oxygen under irradiation through effective singlet-to-triplet transition, since the spin-orbit coupling of Pt contributes to their singlet-to-triplet transition that is able to convert molecular oxygen to singlet oxygen, instead of fluorescence (Scheme 1B).[15,16]

To demonstrate the capacity of Bodiplatin-NPs to generate photothermal effect, we measured their thermal behaviors under 660 nm irradiation at 0.5 W cm−2. Bodiplatin-NPs and Bodiplatin had the fast temperature elevations (ΔT) of ≈21.0 and ≈17.0 °C in 300 s at the concentration of 30 × 10−6 m (Figure 2G), respectively, which were much higher than that of Bodipy (ΔT = 6.0 °C). Moreover, Bodiplatin-NPs exhibited the concentration-dependent temperature elevations, and also generated a temperature increase of 9.0 °C even at a low concentration of 10 × 10−6 m (Figure S12, Supporting Information). Clearly, the platination of BDP core facilitates the generation of photothermal effect in addition to singlet oxygen. Next, their photothermal conversion efficiencies (η) were also measured. Bodiplatin-NPs and Bodiplatin exhibited the preferable photothermal conversion efficiencies of 37.0% and 27.0% as compared to Bodipy (11.0%), respectively (Figure S13, Supporting Information). Remarkably, Bodiplatin-NPs have the enhanced photothermal conversion efficiency owing to their enhanced nonradiative decay within self-assembled nanostructure, which is comparable to those of the existing photothermal agents such as gold nanorods and organic dyes.[17] Moreover, Bodiplatin-NPs also exhibited the shortest fluorescence lifetime of 0.5 ns as compared to those of Bodiplatin (1.3 ns) and Bodipy (4.3 ns) (Figure 2H). It validates that Bodiplatin-NPs have the ultralow radiative transition, confirming that the platination of fluorophore core within self-assembled nanostructure plays a key role for generating both sufficient singlet oxygen quantum yield and enhanced photothermal conversion efficiency, accompanying with minimized fluorescence.[14,15]

Given that Pt can induce remarkable photothermal effect of Bodiplatin-NPs in addition to singlet oxygen, the unoccupied d2,2,2 orbitals of Pt atom might be involved in the communications of electrons in fluorophore core upon light irradiation, and thus density functional theory (DFT) calculation was performed to demonstrate the role of Pt in the generation of the photothermal effect. The structures of energy-minimized calculated Bodiplatin and Bodipy were illustrated as the representative examples according to the DFT calculation, respectively (Figure S14 and S15).[16] Obviously, the molecular orbitals of Bodiplatin were significantly different from those of Bodipy. The electron densities of highest occupied molecular orbital (HOMO, −4.97 eV) and lowest unoccupied molecular orbital (LUMO, −2.89 eV) of Bodipy are primarily localized at the π and π* orbitals in BDP moiety with negligible electronic communications on axial pyridyl moieties (Figure S15, Supporting Information), resulting in the radiative transition of Bodipy for generating fluorescence. However, molecular orbitals of Bodiplatin show that both dπ,2,2 orbital on Pt atom and π* orbital on pyridyl moiety are mainly involved in the LUMO (−4.98 eV), and HOMO (−6.46 eV) are located on the π orbital in BDP moiety (Figure S14, Supporting Information).[18] Consequently, unoccupied dπ,2,2 orbital of square planar Pt(II) can allow the d−d energy band transition, thereby accounting for the non-radiative decay of Bodiplatin and Bodiplatin-NPs, and thereof photothermal effect in addition to singlet oxygen (Scheme 1B). So far, there are only a few bifunctional agents that can achieve the generation of both singlet oxygen and photothermal effect with minimized fluorescence,[16,19] although theranostic nanoparticles have been explored through the coencapsulation of imaging agent and therapeutic agent.[20] The platinated nanostructure with ultralow radiative transition can be considered as a novel approach to generate bifunctional effects of singlet oxygen and photothermal effect for photoinduced cancer therapy.

To demonstrate the cellular uptake of Bodiplatin-NPs, we evaluated their internalization by 4T1 murine breast tumor cells. Bodiplatin-NPs exhibited time-dependent cellular uptakes (Figure S16, Supporting Information), which is advantageous to the generation of concentration-dependent singlet oxygen and photothermal effect in the cells upon light irradiation.[21] The confocal laser scanning microscopy (CLSM) was further employed to observe their intracellular distribution in 4T1 cells stained by LysoTracker Green DND-26 under irradiation or not. Figure 3A shows that Bodiplatin-NPs with red fluorescence had a colocalization percentage of about 90.0% with the lysosomes in the absence of irradiation, indicating an effective endocytosis into the lysosomes upon cell internalization, while Bodiplatin-NPs exhibited a poor colocalization of 32.0% with the lysosomes upon irradiation, suggesting that Bodiplatin-NPs are able to cause the lysosomal disruption upon irradiation.[14] Next, we further evaluated the influence of Bodiplatin-NPs on the lysosomes using acidic residue (AO) staining. The lysosomes in 4T1 cells treated with PBS and Bodipy emitted red fluorescence under irradiation or not, while the red fluorescence was significantly disappeared in the presence of Bodiplatin-NPs and Bodiplatin at the dose of 1.0 × 10−6 m upon irradiation.
Figure 3. A) CLSM image of 4T1 cells stained by Lysotracker Green DND-26 and Hoechst 33342 after 0.5 h incubation with Bodiplatin-NPs under irradiation or not (Scale bar: 25 μm). B) Relative viability of 4T1 cells treated with Bodiplatin-NPs at various doses after 48 h incubation in the presence or absence of Vc under 5 min irradiation or not (660 nm, 0.5 W cm$^{-2}$). C) Plasma concentration of Pt from Bodiplatin-NPs and Bodiplatin at different time after intravenous administration at the dose of 10.0 μmol kg$^{-1}$. D) Ex vivo biodistribution of Pt at various tissues of the mice treated with Bodiplatin-NPs and Bodiplatin at the dose of 10.0 μmol kg$^{-1}$ at 24 h post-injection (student’s t-test, **p < 0.01), respectively. E) Infrared thermography, and F) temperature elevation at the tumors of the mice injected with Bodiplatin-NPs and Bodiplatin at the doses of 5.0, 7.0, and 10.0 μmol kg$^{-1}$ at 24 h post-injection under 5 min irradiation (660 nm, 0.5 W cm$^{-2}$), respectively. G) DHE staining at the tumors of the mice injected with Bodiplatin-NPs and Bodiplatin at the dose of 7.0 μmol kg$^{-1}$ in the presence or absence of Vc at 24 h post-injection under 660 nm irradiation at 0.5 W cm$^{-2}$ for 5 min (Scale bar: 100 μm).
Bodiplatin-NPs also exhibited a remarkable cytotoxicity of $3.0 \times 10^{-6}$ M in the absence of irradiation (Figure S19, Supporting Information), indicating that they are a nontoxic agent owing to their negligible dark cytotoxicity, and still cause severe photocytotoxicity under irradiation. Interestingly, their cell viability was significantly increased ($16.0 \times 10^{-6}$ M IC$_{50}$) in the presence of ROS-scavenger Vitamin C (Vc) under irradiation, indicating that the photoinduced cytotoxicity is compromised owing to the absence of photodynamic damage. Therefore, singlet oxygen from Bodiplatin-NPs distinctly contributes to the photocytotoxicity in addition to photothermal effect. Distinctly, Bodiplatin-NPs are able to provide remarkable photoinduced cytotoxicity even at a relatively low concentration, owing to the synergy between singlet oxygen and photothermal effect. To further demonstrate the applicability of Bodiplatin-NPs at a clinically applied irradiation density, we further evaluated their cytotoxicity under 0.15 W cm$^{-2}$ irradiation (15 min, 660 nm) (Figure S20, Supporting Information). Bodiplatin-NPs also exhibited a remarkable cytotoxicity of $3.0 \times 10^{-6}$ M IC$_{50}$ under 0.15 W cm$^{-2}$ irradiation, while they only had the sole PTT cytotoxicity of $110.0 \times 10^{-6}$ M IC$_{50}$ in the presence of ROS-scavenger Vc. Therefore, a relatively low irradiation still causes slightly reduced PTT/PDT cytotoxicity, but triggers distinctly decreased photothermal cytotoxicity. Moreover, the photoinduced cell damage of Bodiplatin-NPs was further validated using Annexin-V/PI staining. Bodiplatin-NPs resulted in the enhanced late apoptosis/necrosis under 0.5 W cm$^{-2}$ irradiation (Figure S21, Supporting Information), confirming that Bodiplatin-NPs have a strong capacity to generate in vivo singlet oxygen at tumor under irradiation for PDT treatment in addition to the potent hyperthermia.

To demonstrate the in vivo anticaner efficacy, Bodiplatin-NPs were administrated into the mice bearing 4T1 tumor at the dose of $7.0 \mu$mol kg$^{-1}$ through a single-dose intravenous injection, followed by the irradiation on the tumors at 24 h post-injection. Then, the tumor volumes were measured during subsequent 30 d (Figure 4A). PBS as a control had a 30-fold increase of tumor volumes regardless of irradiation, indicating that the light irradiation has no distinct influence on the tumor growth. Bodiplatin-NPs and Bodiplatin in the absence of irradiation also exhibited the similar tumor growth behaviors to those of PBS, suggesting that Bodiplatin-NPs and Bodiplatin can act as the nontoxic agents without irradiation. Interestingly, Bodiplatin resulted in the tumor ablation under irradiation, but still exhibited significant tumor regrowth at 7 d post-irradiation (Figure 4A,B). More importantly, Bodiplatin-NPs exhibited the total tumor ablation without any regrowth under irradiation, while Bodiplatin-NPs also had a remarkable tumor regrowth in the presence of ROS-scavenger Vc in the tumor. Obviously, the combination of hyperthermia and ROS from Bodiplatin-NPs causes the total tumor ablation (Scheme 1C), while only PDT treatment is unable to ablate all the tumors in the absence of photodynamic damage. Hence, the ROS-mediated PDT treatment plays a key role for achieving the synergistic therapy with tumor ablation. In particular, the potent hyperthermia of Bodiplatin-NPs with the temperature elevation of 21.5 °C at tumor can act as a prerequisite for achieving the tumor ablation.
without regrowth, while the tumor temperature increase of 12.0 °C from Bodiplatin is not enough to destruct the residual tumor cells for avoiding tumor regrowth (Figure 3D). In addition, we further evaluated the in vivo efficacy of Bodiplatin-NPs under 0.15 W cm⁻² irradiation (Figure S22, Supporting Information). It shows that Bodiplatin-NPs still exhibited remarkable tumor inhibition effect under 0.15 W cm⁻² irradiation, although not all the tumors were ablated. Reasonably, the lower irradiation density causes less photoconversion into both singlet oxygen and photothermal effect, thereby accounting for the decreased anticancer efficacy.

In addition, Bodiplatin-NPs with the combination of PDT and PTT treatments might also demand a decreased tissue oxygen depletion as compared to conventional PS owing to the presence of the hyperthermia, potentially facilitating their anticancer efficacy. To further confirm the anticancer efficacy, hematoxylin & eosin (H&E) staining was applied to examine the ability of Bodiplatin-NPs to cause the tumor damage under irradiation. Bodiplatin-NPs were found to cause severe hemorrhagic inflammation and destructive cell necrosis in the tumor at 6 h post-irradiation (Figure 4C and Figure S24, Supporting Information), indicating a desirable ability to destruct the tumor cells as compared to Bodiplatin. In contrast, PBS showed no distinct tumor damage regardless of irradiation, and Bodiplatin-NPs also exhibited no significant influence on the normal tissues such as heart, liver, spleen, lung, and kidney (Figure S25, Supporting Information). In addition, we also did not observe remarkable skin damage under 0.15 or 0.5 W cm⁻² irradiation, possibly owing to relatively low hyperthermia (4.5–7.5 °C) from the tissue itself within short irradiation time.

To demonstrate the in vivo clearance of Bodiplatin-NPs, their distribution at various tissues were monitored during 21 d post-injection (Figures S26, Supporting Information). Bodiplatin-NPs were mainly distributed into some normal tissues including liver and kidney at 24 h post-injection, and then the distribution of Bodiplatin-NPs at various normal tissues were gradually decreased during 21 d post-injection, indicating that Bodiplatin-NPs are gradually eliminated from the normal tissues. Moreover, the blood chemistry assay of Bodiplatin-NPs was further performed to evaluate their potential toxicity. The levels of liver function markers (ALP, AST, and ALT) and kidney function marker (urea) exhibited no remarkable change during 21 d post-injection (Figure S27, Supporting Information), suggesting that Bodiplatin-NPs have no distinct damage on the normal tissues. Consequently, bifunctional Bodiplatin-NPs possess an ideal capacity to achieve photoinduced cancer therapy, owing to their multiple advantages including enhanced photostability, effective intracellular translocation, preferable biodistribution,
synergistic PDT/PTT efficiency under single-wave light irradiation, as well as reduced demand of tissue oxygen.\footnote{[1]} In summary, platinated fluorophore (boron dipyrromethene) core has been synthesized to fabricate self-assembled Bodiplatin-NPs with ultralow radiative transition, which possess both enhanced singlet-to-triplet transition and nonradiative decay through their spin-orbit coupling and unoccupied d,\textit{z},d,\textit{t} orbitals under light irradiation. Bodiplatin-NPs generate both abundant singlet oxygen and effective photothermal conversion upon light irradiation. In particular, Bodiplatin-NPs exhibit the collective characteristics including red-shifted absorbance, enhanced resistance to photobleaching, intracellular translocation from lysosomes to cytoplasm, preferable tumor accumulation, reduced tissue oxygen depletion as well as bifunctional therapeutic effects under single-wave light irradiation, facilitating remarkable photoinduced cell damage and subsequent synergy between photodynamic and photothermal therapy even at a relatively low irradiation density. Interestingly, Bodiplatin-NPs also have remarkable absorption in the range of 700–750 nm, potentially allowing single-wave near-infrared light with deeper penetration depth to trigger PTT/PDT treatments. Our proof-of-concept design of self-assembled nanostructure with platinated fluorophore core represents a general and versatile approach for photoinduced tumor ablation.

**Experimental Section**

Detailed experimental materials and methods can be found in the Supporting Information.

**Supporting Information**

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

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