Supporting Information

Aggregation-Induced Emission (AIE)-Active Metallacycles with Near-infrared Emission for Photodynamic Therapy

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1. Experimental Section

1.1 Materials

All the chemicals and reagents were commercially available and used as received without further purification. Tetrakis-(triphenylphosphine)-palladium [$Pd(PPh_3)_4$], 4-(7-bromobenzo[*c*] [1,2,5]thiadiazol-4-yl)-N,N-bis(4-methoxyphenyl)aniline, 4-(pyridin-4-yl)-N-(4-(pyridin-4-yl)phenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline and Hoechst 33342 were purchased from Alfa Aesar. 1,2-Distearoyl-sn-glycero-3-phosphoethanolamine-N-[methoxy(poly-ethylene glycol)-2000] (DSPE-PEG_{2000}) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.

1.2 Characterization and Measurement

^1H NMR and ^{13}C NMR spectra of DTPABT-P, ^1H NMR spectrum and ^{31}P NMR spectra of DTPABT-MC-R dissolved in DMSO-d_6 were measured on a Bruker Advance 600 MHz and the internal reference is tetramethylsilane (TMS, δ= 0 ppm). UV-Vis spectra were measured by using a Shimadzu UV-2250 spectrophotometer. Photoluminescence (PL) spectra, transient PL decay curves and photoluminescence quantum yields (PLQYs) were measured on a FLS980 transient steady-state fluorescence spectrometer of Edinburgh apparatus. The hydrodynamic sizes and distributions were measured at room temperature by using a Malvern Zetasizer Nano ZS90. Transmission electron microscopic (TEM) images were captured by JEOL-2100 electron microscope. Confocal laser scanning microscopic images were recorded by Leica SP8.

1.3 Preparation of nanoparticles

DTPABT-MC-R NPs were prepared by a commonly used re-precipitation method.[1] DTPABT-MC-R (1 mg) and DSPE-PEG_{2000} (4 mg) were dissolved in DMSO (0.1 mL) and the resulted solution was then quickly injected into water (5 mL) under stirring. After 1 hour, nanoparticles were successfully prepared and stored for the following application.

1.4 Cell viability assay and cell imaging

A standard CCK-8 assay was conducted to determine cell cytotoxicity.[2] 4T1 cells were cultured in Dulbecco's modified eagle medium (DMEM) at 37 °C in a humified atmosphere with 5% CO_2. They were then seeded in 96-well plates at a density of 1×10^5 per well for ~24 h to adherent under the same incubation conditions. After that, cells were then treated with different concentrations of nanoparticles for 24 hours, followed with the addition of CCK-8 (1 mg/mL in medium, 100 μL/well) after removing the supernatant. Cell viability was finally determined by a microplate reader at 450 nm.

For cell imaging, HeLa cells were firstly seeded in the culture dishes with a density of 5×10^4 mL^{-1}. After adherent, the supernatant was removed and DTPABT-MC-R NPs (15 $\mu g\cdot mL^{-1}$ in DMEM) was added to cells for 12 h. Then, hoechst 33342 was also added to stain the cells for 5 min. After being cleaned by PBS, living HeLa cells was imaged by using a confocal laser scanning microscope (CLSM).

1.5 Photodynamic performance test

HeLa cells were seeded in the culture dishes with a density of 1×10^5 mL^{-1}. After adherent, the supernatant was removed and DTPABT-MC-R NPs (15 $\mu g\cdot mL^{-1}$ in DMEM) was firstly added to cells for 12 h. Then, DCHF-DA was added to cultivate the cells for 20 min. After being cleaned by PBS, HeLa cells imaging was performed by using a CLSM under the conditions of darkness and the white light irradiation (5 $mW\cdot cm^{-2}$, 5min).

2. Synthesis

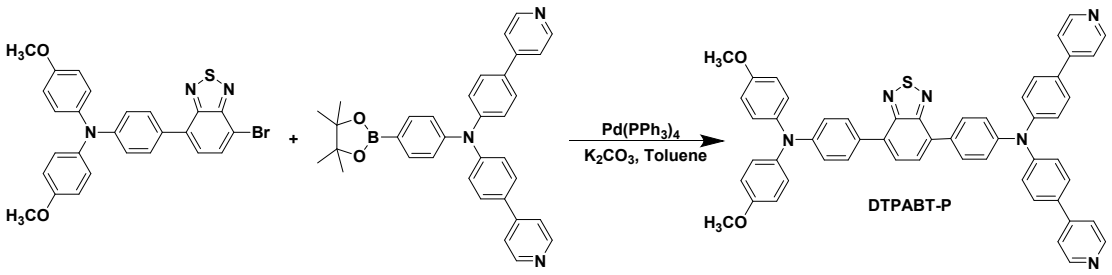
2.1 Synthesis of DTPABT-P

Tetrakis-(triphenylphosphine)-palladium [$Pd(PPh_3)_4$] (14 mg) and potassium carbonate (K_2CO_3, 2 M, 7.5 mL) were added to a solution of 4-(7-bromobenzo[c] [1,2,5]thiadiazol-4-yl)-N,N-bis(4-methoxyphenyl)aniline (0.310 g, 0.6 mmol) and 4-(pyridin-4-yl)-N-(4-(pyridin-4-yl)phenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (0.315 g, 0.6 mmol) in a mixture of toluene (180 mL) and ethanol (7.5 mL) under nitrogen. After stirring for 20 hours at 80 °C, the reaction was quenched with water (30 mL). Then the mixture was then extracted with dichloromethane (DCM) for three times (3 × 30 mL), and the obtained organic solution

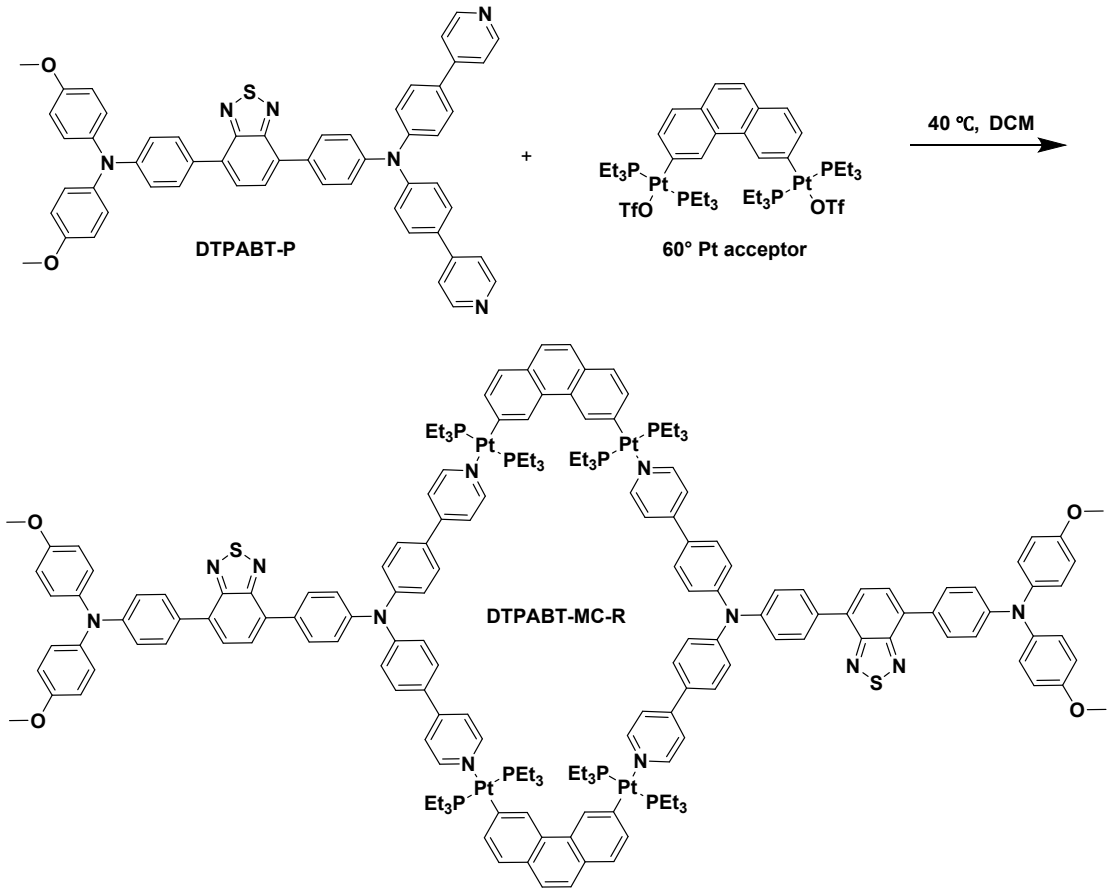
was washed with water (3 × 40 mL). After removing solvent, the crude product was purified by column chromatography to obtain pure DTPABT-P as red solid (0.3 g, 60%). ^{1}H NMR (600 MHz, DMSO) δ: 8.63 (d, *J* = 5.3 Hz, 4H), 8.06 (d, *J* = 8.6 Hz, 2H), 7.94 (d, *J* = 7.5 Hz, 1H), 7.90 (d, *J* = 8.7 Hz, 2H), 7.87 (d, *J* = 7.4 Hz, 1H), 7.85 (d, *J* = 8.6 Hz, 4H), 7.73 (d, *J* = 6.1 Hz, 4H), 7.30 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 4H), 7.12 (t, *J* = 6.1 Hz, 4H), 6.97 (d, *J* = 8.9 Hz, 4H), 6.90 (d, *J* = 8.7 Hz, 2H), 3.77 (s, 6H). ^{13}C NMR (150 MHz, DMSO) δ: 151.48, 149.48, 149.35, 144.64, 144.31, 143.55, 141.80, 135.74, 128.54, 128.28, 127.39, 126.49, 125.57, 125.03, 123.96, 123.39, 123.22, 122.36, 122.15, 122.06, 120.18, 119.75, 116.43, 114.91, 110.05, 50.78.

2.2 Synthesis of DTPABT-MC-R

DTPABT-P (50 mg) and 60° Pt acceptor (79.89 mg) were added in a solution of dichloromethane (DCM) (30 mL). Then, the mixture was stirred for 12 hours at 40 ^{o}C. After that, most of the DCM was removed and diethyl ether was added to form the precipitation. Repeat this operation twice to purify product. After the filtration, DTPABT-MC-R as red solid was obtained (106.5 mg, 95%). ^{1}H NMR (600 MHz, DMSO) δ: 8.88 (d, J = 5.2 Hz, 2H), 8.84 (d, J = 5.1 Hz, 2H), 8.64 (d, J = 22.1 Hz, 2H), 8.20 (d, J = 8.1 Hz, 2H), 8.12 (d, J = 4.6 Hz, 2H), 8.09 (d, J = 4.8 Hz, 2H), 8.03 (d, J = 7.8 Hz, 4H), 7.94 (d, J = 8.2 Hz, 4H), 7.67 (s, 4H), 7.63 (s, 2H), 7.44 (d, J = 8.1 Hz, 2H), 7.39 (d, J = 8.0 Hz, 4H), 7.15 (d, J = 8.8 Hz, 4H), 6.99 (d, J = 8.9 Hz, 4H), 6.93 (d, J = 8.4 Hz, 2H), 3.79 (s, 6H), 1.37 (s, 24H), 1.14 (dd, J = 15.7, 7.8 Hz, 36H).



Scheme S1. Synthetic route to DTPABT-P.



Scheme S2. Synthetic route to DTPABT-MC-R.

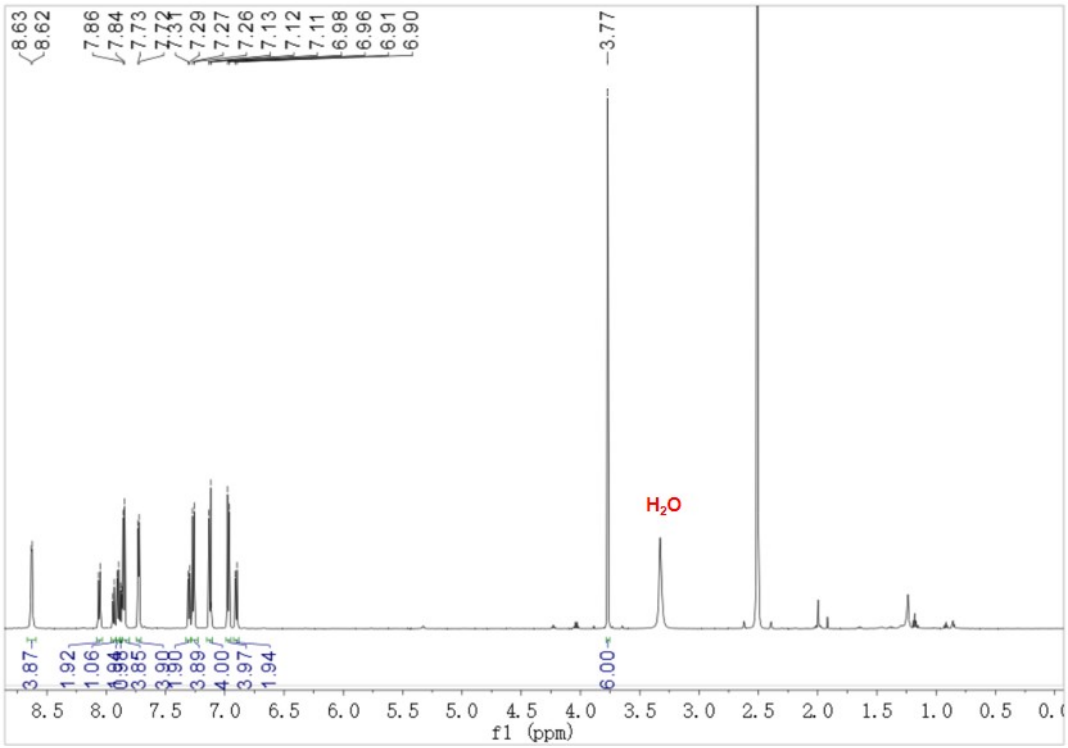


Fig S1. ^{1}H NMR spectrum of DTPABT-P.

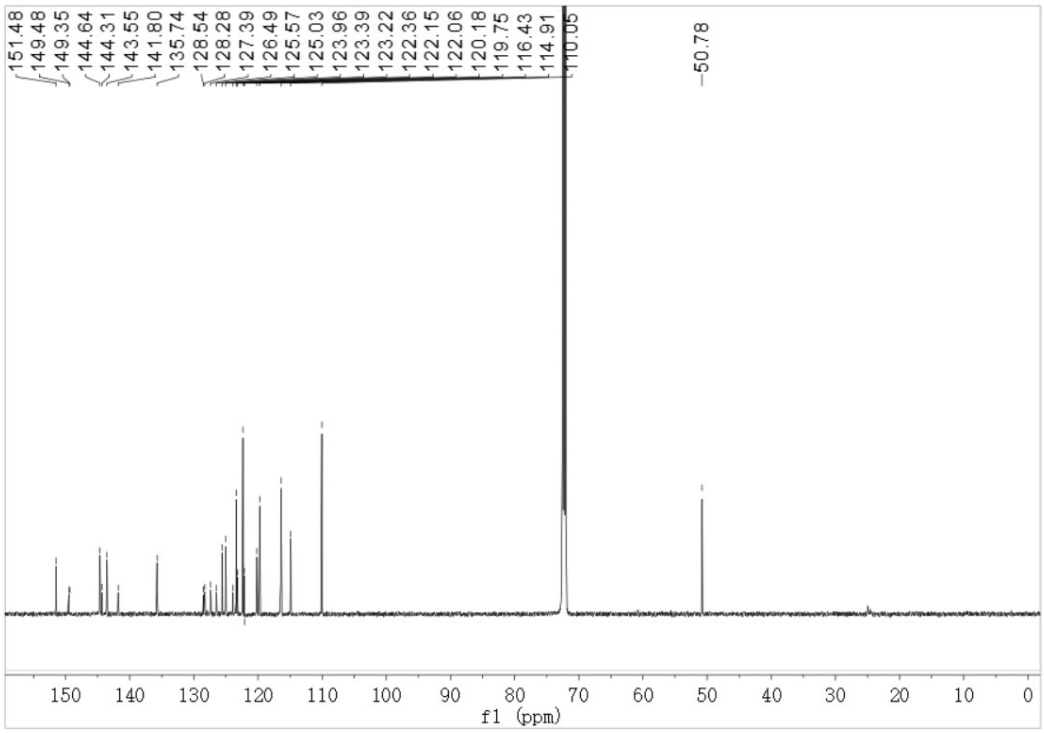


Fig S2. ^{13}C NMR spectrum of DTPABT-P.

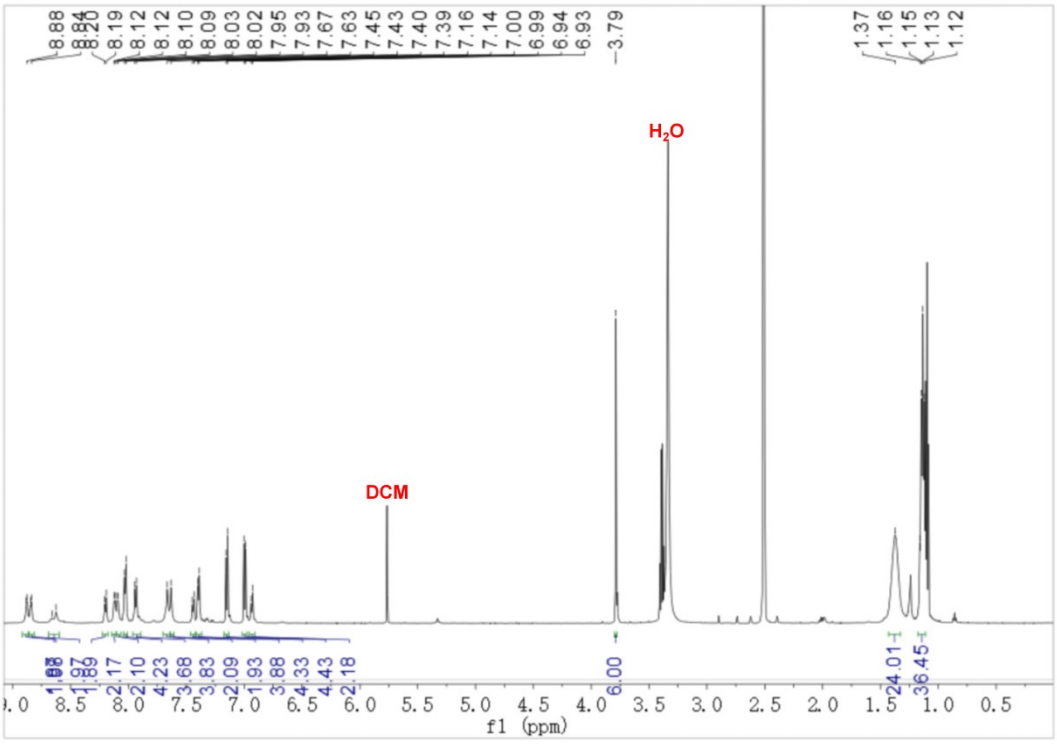


Fig S3. ^{1}H NMR spectrum of DTPABT-MC-R.

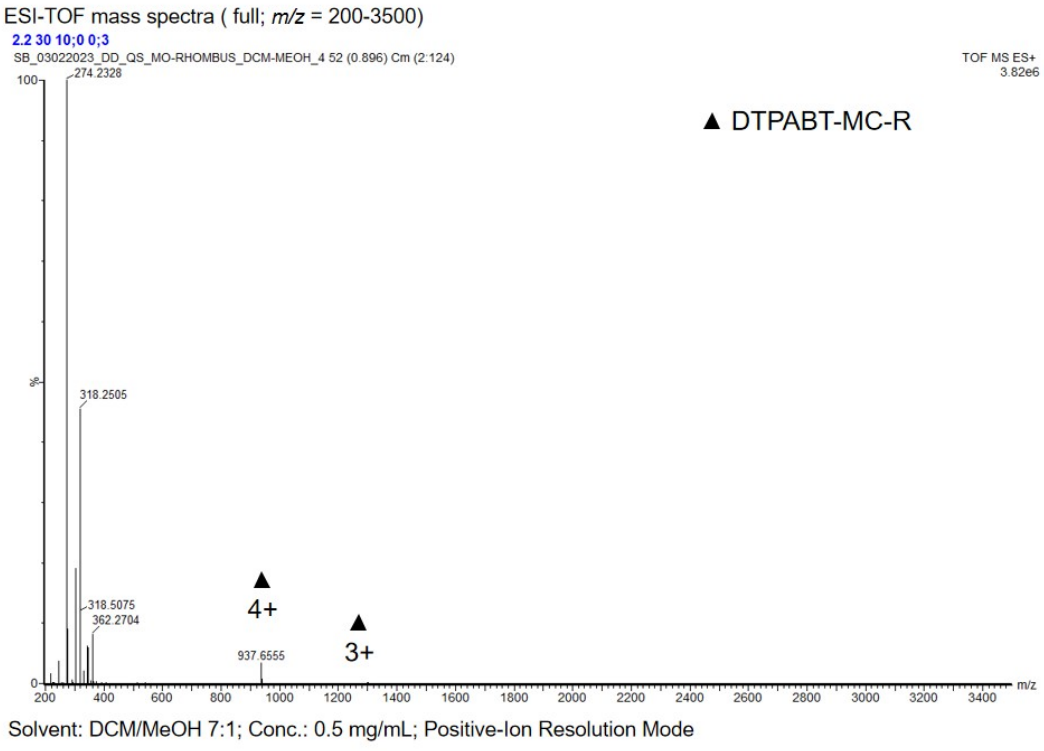


Fig S4. ESI-TOF-MS spectra of DTPABT-MC-R.

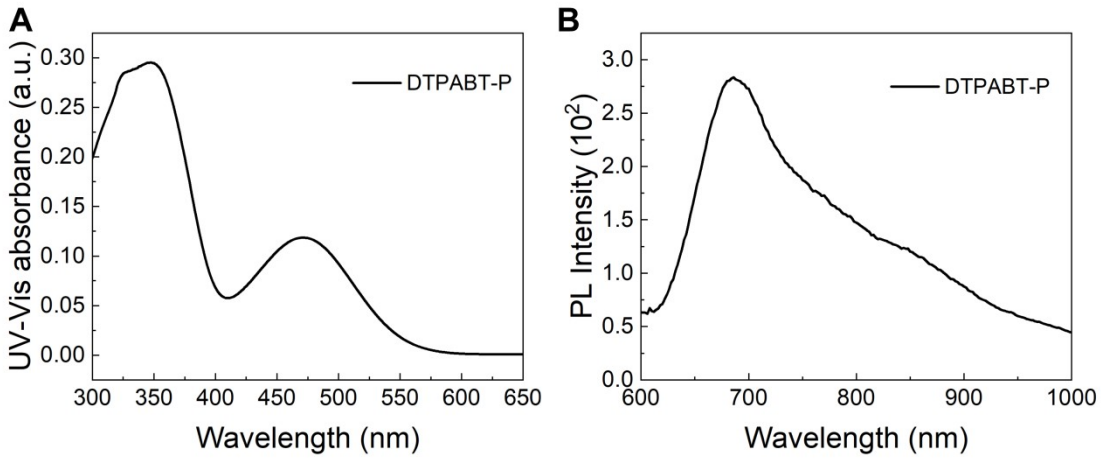


Fig S5. UV-Vis absorption (A) and PL spectra (B) for DTPABT-P in DMSO solution.

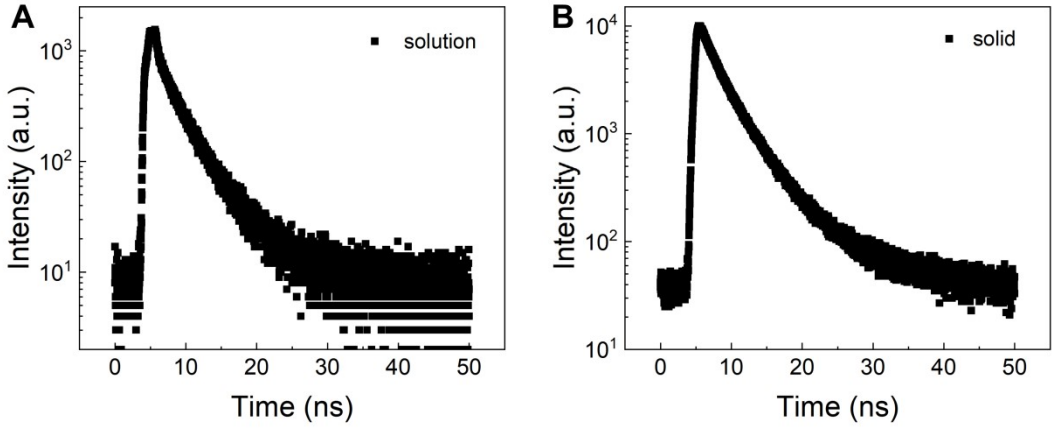


Fig S6. Transient PL decay curves of DTPABT-MC-R in solution (A) and in solid (B).

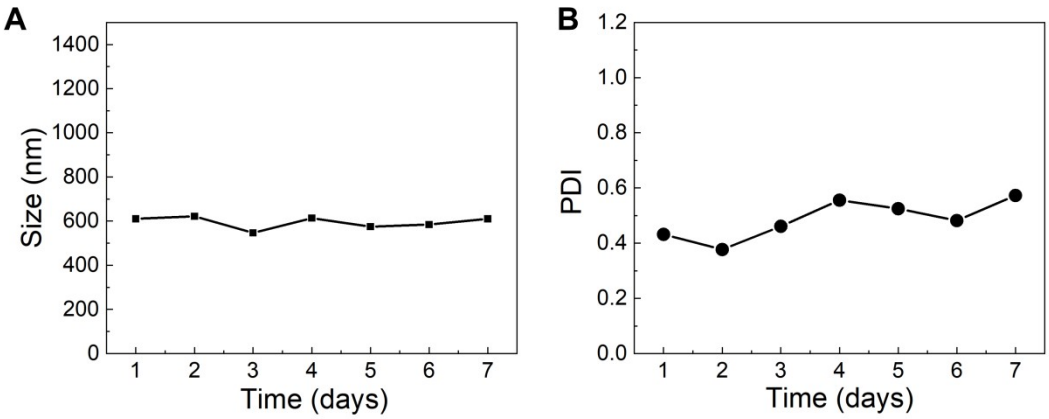


Fig S7. The size (A) and PDI (B) of DTPABT-MC-R NPs over 7 days.

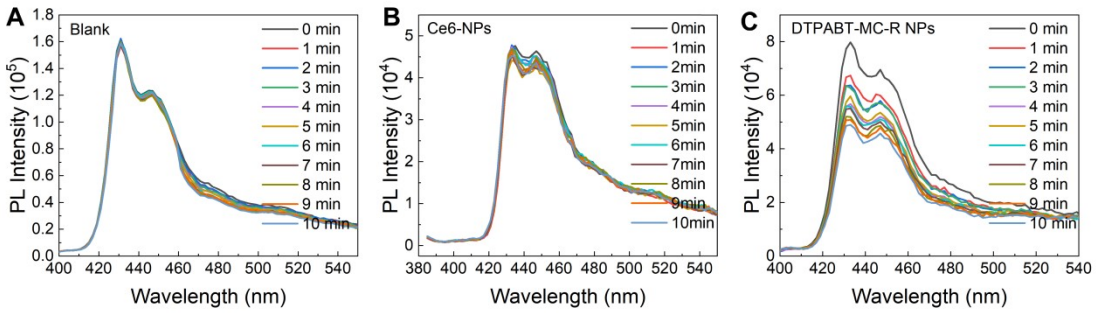


Fig S8. PL spectra of DMA dispersed in water (A), and in water containing Ce6 NPs (B), DTPABT-MC-R NPs (C) under white light irradiation (400-800 nm, 5 mW·cm^{-2}).

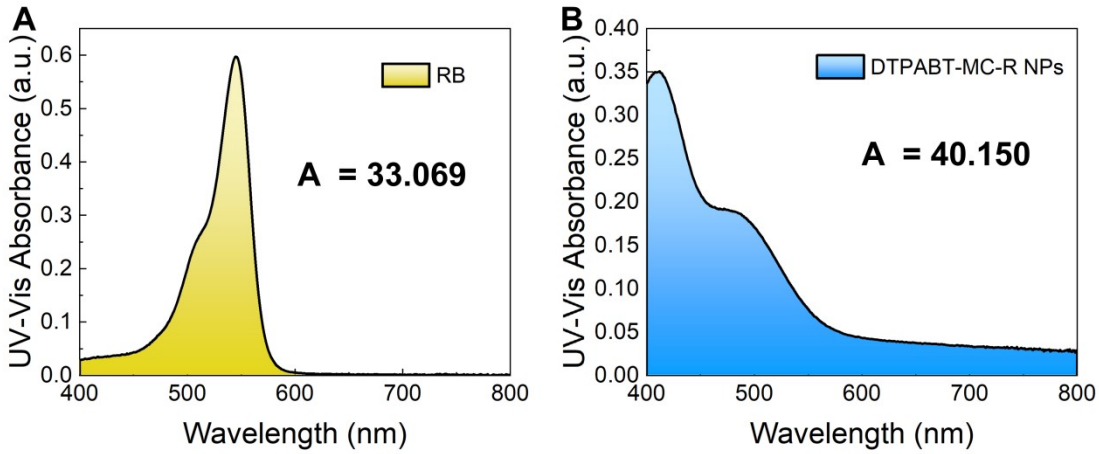


Fig S9. UV-Vis absorbance spectrum of RB (A), and DTPABT-MC-R NPs NPs (B), A stands for area of integration.

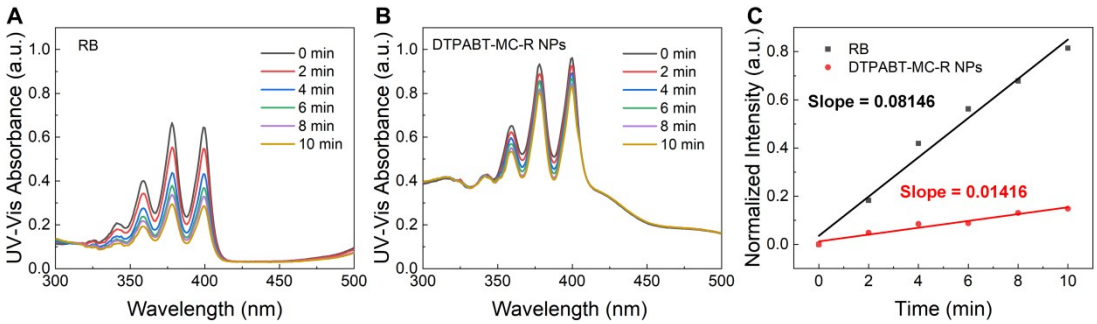


Fig S10. UV-Vis absorption spectra of ABDA dispersed in RB solution (A), and in DTPABT-MC-R NPs (B) under white light irradiation (400-800 nm, 5 mW·cm^{-2}); Decomposition rate of ABDA with RB and DTPABT-MC-R NPs (C).

Table S1. Photophysical properties of DTPABT-MC-R.

Compounds	Absorbance (nm)	ε ($\times10^5$ L/ mol·cm)	Emission[a] (nm)	Stokes' shift (nm)	PLQYs[a]/ PLQYs[b] (%)	τ^a / τ^b (ns)	k_r^a/k_r^b ($\times10^7 s^{-1}$)	k_{nr}^a/k_{nr}^b ($\times10^7 s^{-1}$)
DTPABT-MC-R	406	0.66	695	289	0.14/ 4.92	3.46/ 3.17	0.04/ 1.55	28.86/ 30.00

[a]Measured in DMSO solution; [b]Measured in solids.

References

1. G. D. Liang, J. W. Y. Lam, W. Qin, J. Li, N. Xie, B. Z. Tang, *Chem. Commun.*, 2014, 50, 1725.

2. W. Becker, J. Microsc, 2012, 247, 119.