Supporting Information

Evoking Photothermy by Capturing Intramolecular Bond Stretching Vibration-Induced Dark-State Energy

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Structural characterization

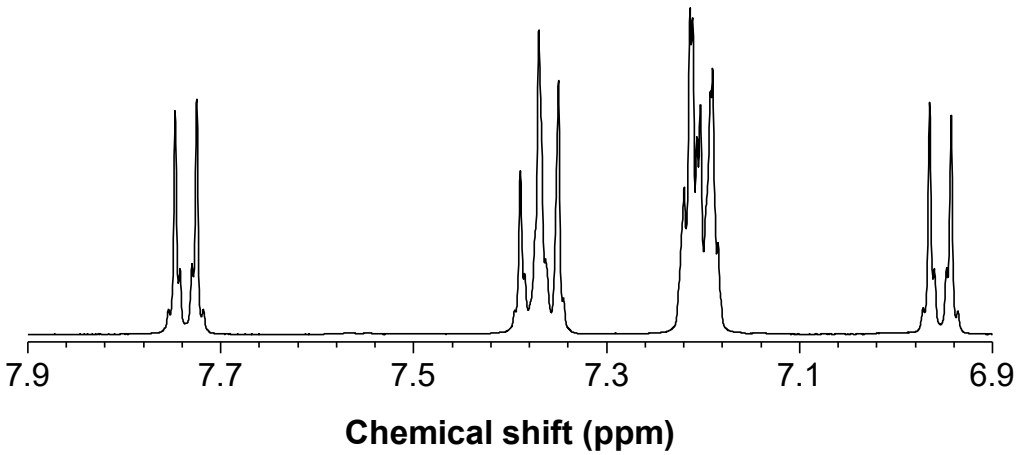

Figure S1. ^{1}HNMR spectrum of DCP-TPA in CD_2Cl_2.

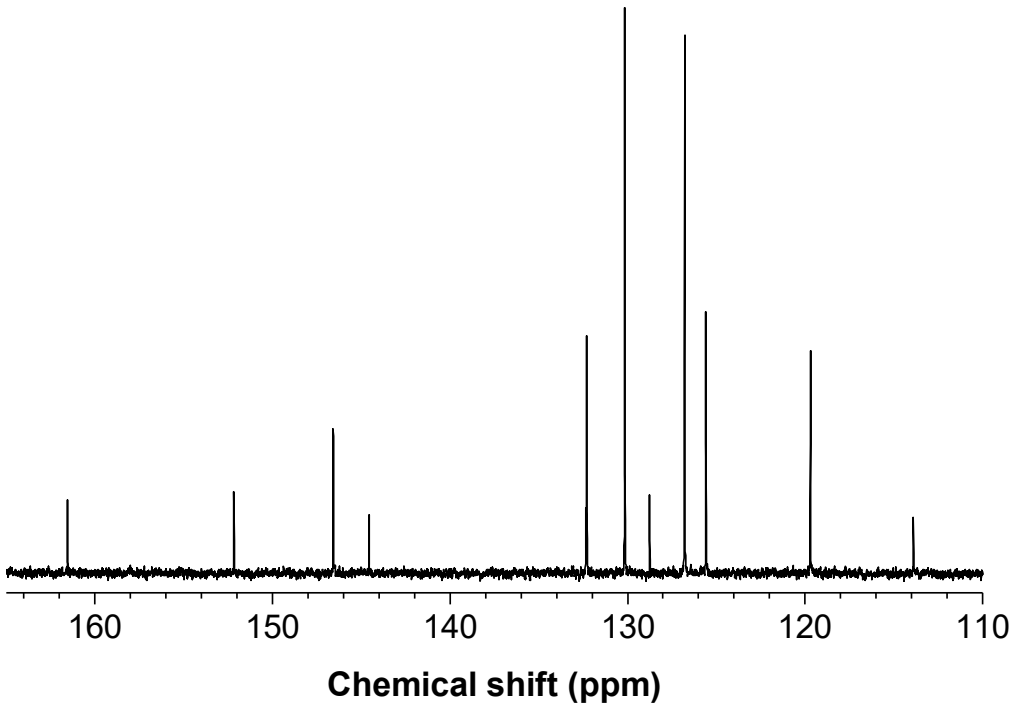

Figure S2. ^{13}C spectrum of DCP-TPA in CD_2Cl_2.

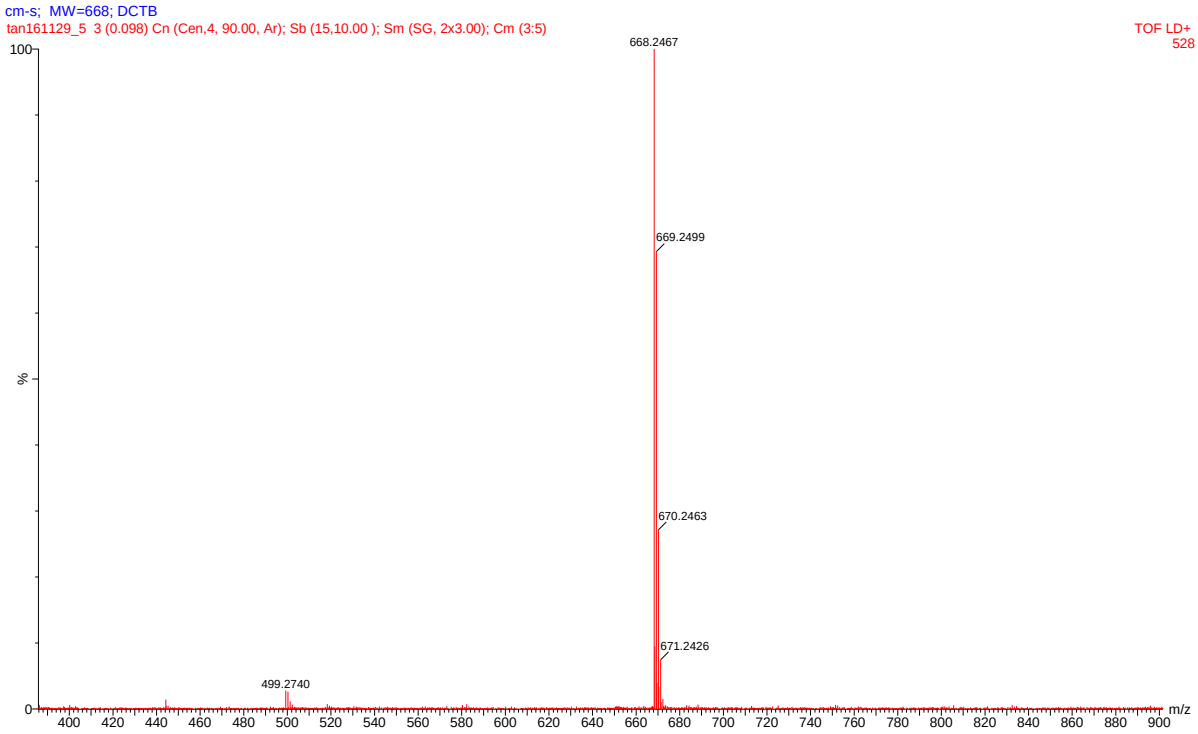

Figure S3. HRMS spectrum of DCP-TPA.

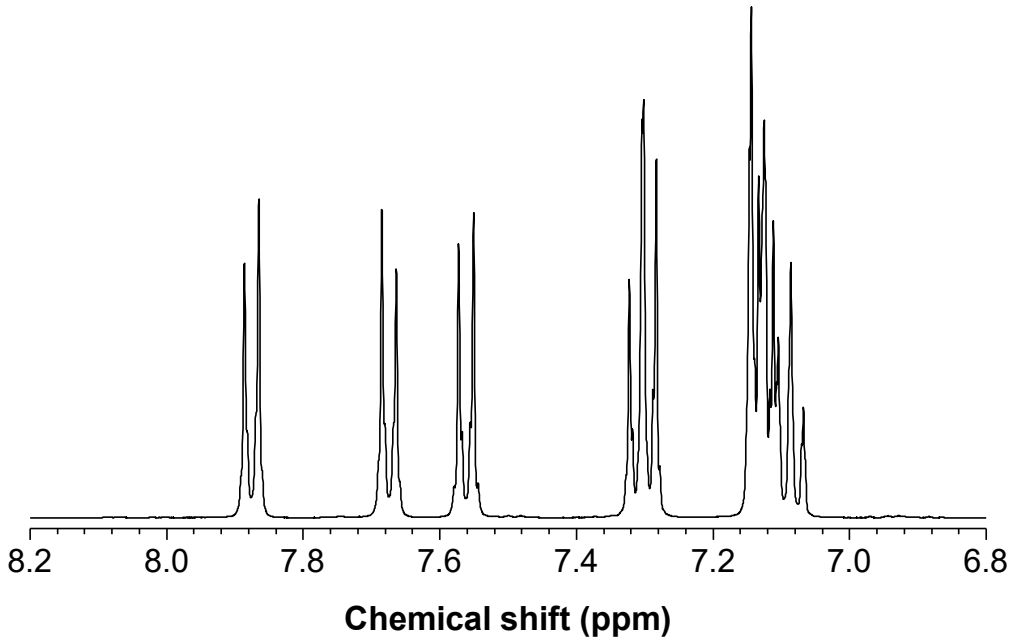

Figure S4. ^{1}H NMR spectrum of DCP-PTPA in CD_2Cl_2.

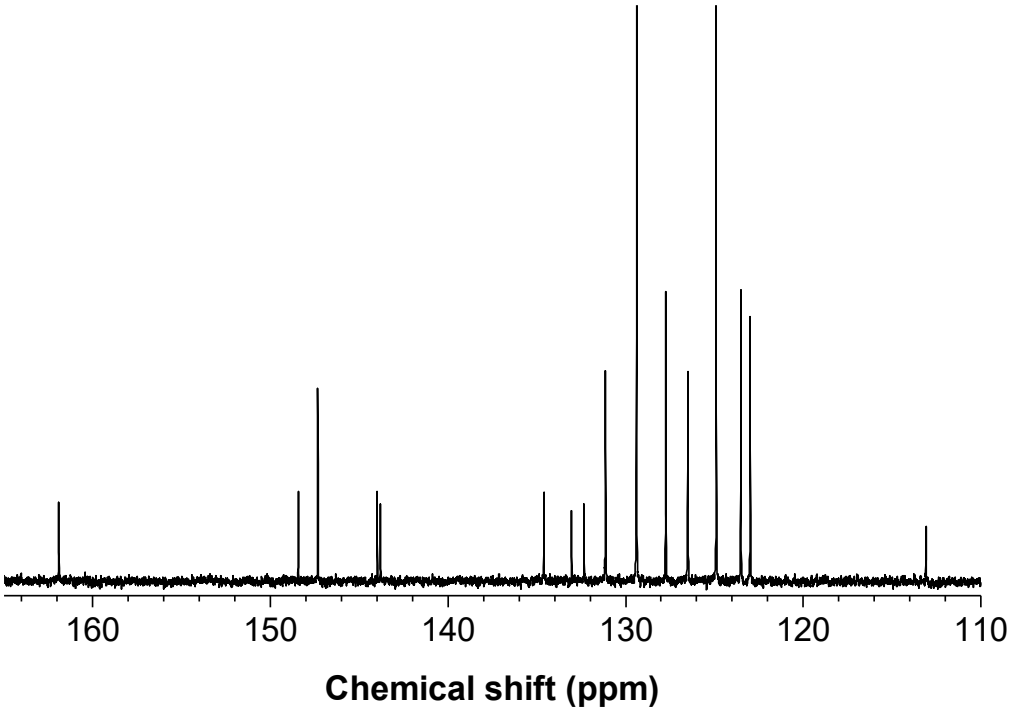

Figure S5. ^{13}C NMR spectrum of DCP-PTPA in CD_2Cl_2.

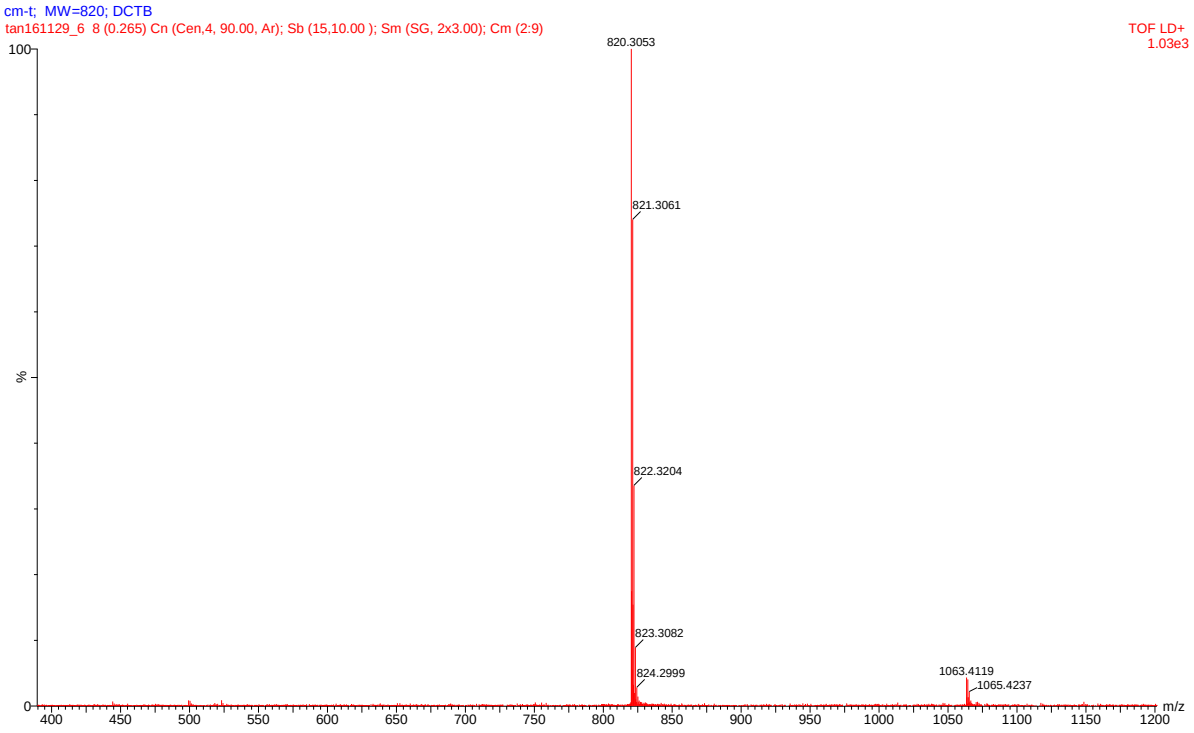

Figure S6. HRMS spectrum of DCP-PTPA.

UV-vis and photoluminescence spectra

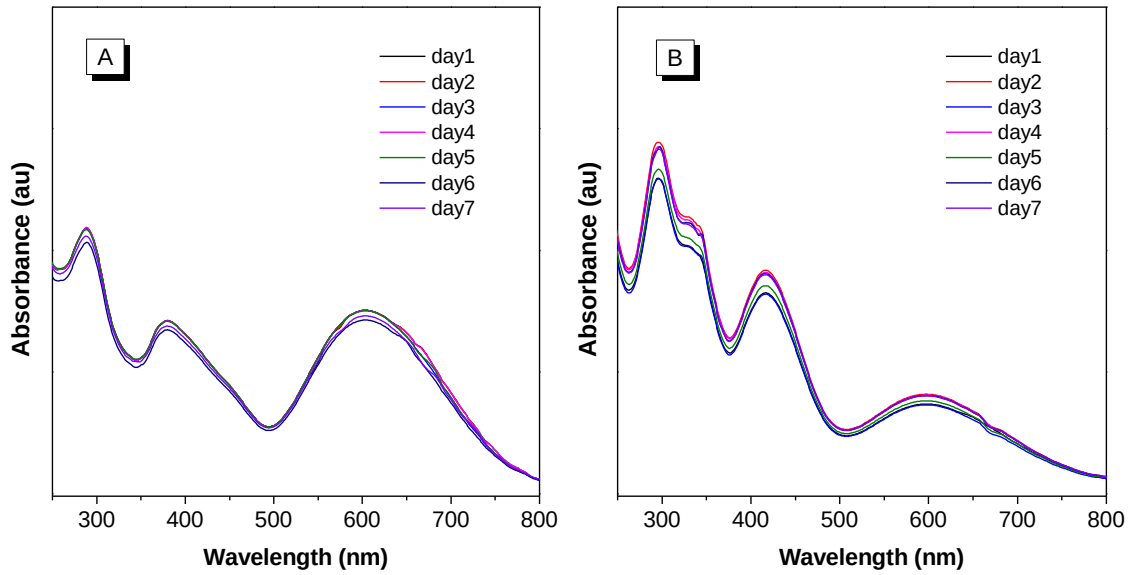

Figure S7. UV-vis spectra of (A) DCP-TPA NPs and (B) DCP-PTPA NPs during one week in aqueous solution, the concentration based on dyes is 40 μM.

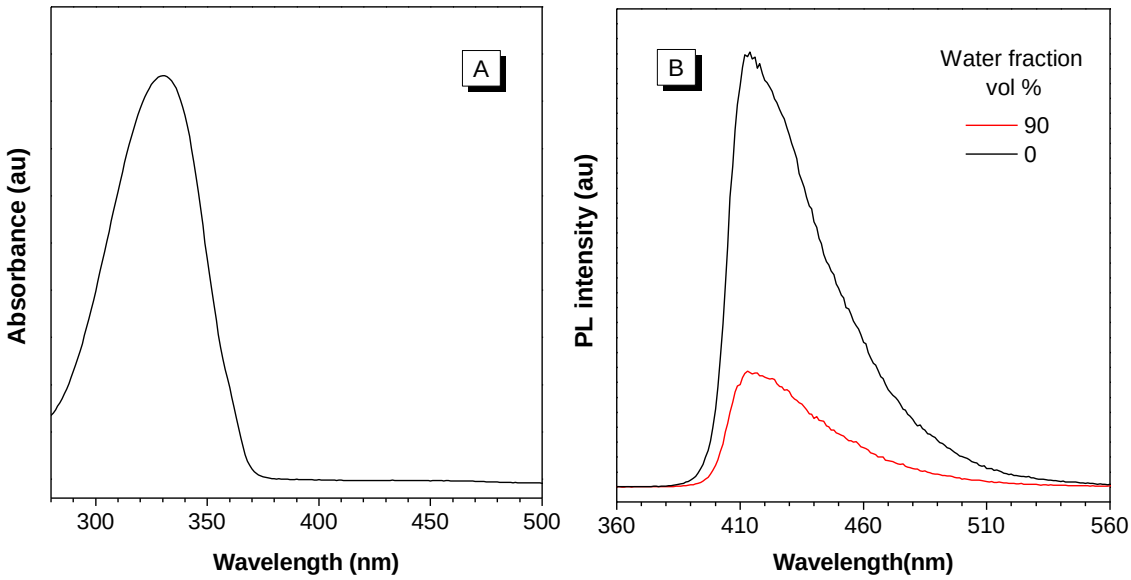

Figure S8. (A) UV absorption spectrum of **3** in DMSO. (B) PL spectra of **3** in DMSO and DMSO/water mixture with a 90% water content, λ_{ex} = 330 nm. The concentration = 10 μM.

Theoretical analysis of compounds

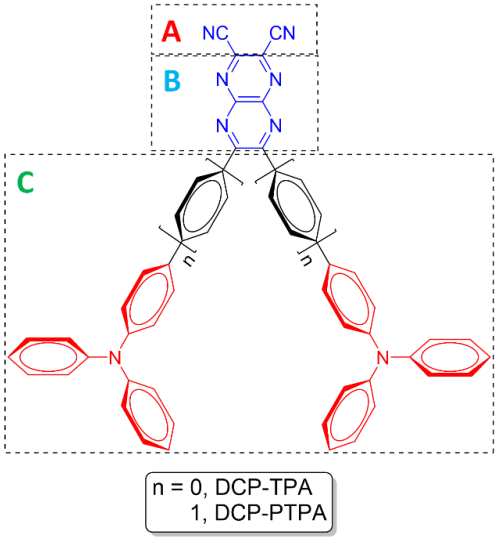

Figure S9. Divided structural units in DCP-TPA and DCP-PTPA. The A, B and C show different part of the molecules, which may have different structural attributes and movements.

Cytotoxicity evaluation

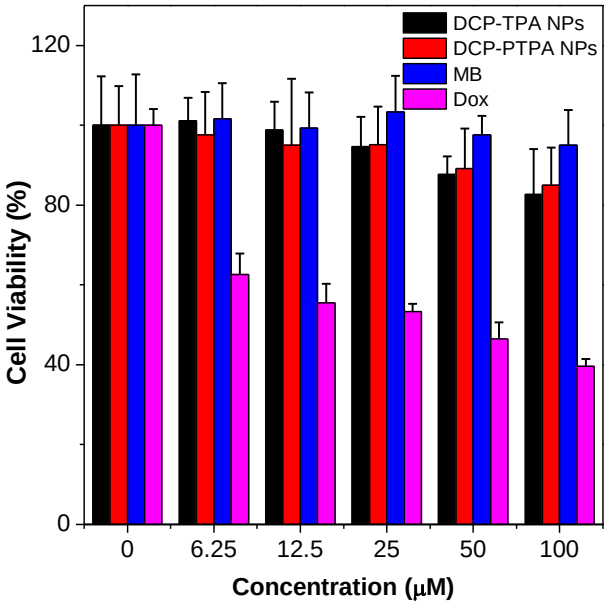

Figure S10. Cytotoxicity of DCP-TPA NPs and DCP-PTPA NPs at different concentrations based on DCP-TPA/DCP-PTPA against 4T1 cancer cells at 24 h, while the cytotoxicity of Doxorubicin (Dox) and MB are evaluated as positive and negative controls.

Reorganization energy contributions

Table S1. Reorganization energy mainly contributed by bond stretch (↔) and changes of dihedral angle (↻) of each part of molecules.

DCP-TPA						DCP-PTPA					
A		B		C		A		B		C	
↔	↻	↔	↻	↔	↻	↔	↻	↔	↻	↔	↻
9	26	1111	29	215	64	11	58	1036	32	1031	451