Large Stokes Shift by Increasing Intramolecular Charge Transfer for High Signal-to-Background Ratio Bioimaging

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Contents

1. Materials

All materials were used directly without further purification. citric acid, (1S,2S)-(-)-1,2-Diphenyl-1,2-ethanediamine, N,N'-Carbonyldiimidazole, Dimethylamine, Tetrahydrofuran, ethyl acetate, petroleum ether, Magnesium sulfate anhydrous, dichloromethane(DCM), methanol, N-Bromosuccinimide, Sodium Methoxide, Silver carbonate, Potassium phosphate, 4-Boric acid triphenylamine, 2-thiophene boronic acid, Tetrakis(triphenylphosphine)palladium, Phenylboronic acid, 4-(Dimethylamino) phenylboronic acid and (4-(Bis(4-methoxyphenyl)amino)phenyl)boronic acid were purchased from Energy Chemical. 3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT), dimethyl sulfoxide (DMSO) and 1,4-dioxane were purchased from BT Reagent. Penicillin-streptomycin was purchased from Macgene (China). RPMI-1640 and FBS were purchased from Gibco (USA). Lyso-Tracker Green, Phosphate buffer solution, 4% paraformaldehyde tissue fixative solution, Dimethyl sulfoxide (Cell level) and Agarose were purchased from Beijing Solarbio Science and Technology Co., Lta.

2. Equipment

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 400 spectrometer. High resolution mass spectra (HRMS) were collected using a Finnigan Biflex III mass spectrometer. The ultraviolet-visible spectra were collected on the Thermo Fisher UV-2700 spectrophotometer. The FL emission spectra were collected on the HORIBA FluoroMax-4 spectrofluorometer. Record cell imaging using a confocal laser PL microscope (Zeiss LSM 980). *In vivo* imaging was measured on IVIS lumina series III. Measure cytotoxicity using BIO-RAD enzyme-linked immunosorbent assay (ELISA) reader. Measure the particle size of nanoparticles using a BeNano 180 Zeta particle size analyzer.

3. The density functional theory (DFT) calculations

DFT calculations were performed on the Gaussian 09. program. The geometries of molecular were optimized with B3LYP/6-311g(d)method, and then the HOMO and LUMO energy level parameters of these compounds were calculated based on their ground state geometry.

4. AIE property test

Firstly, a certain amount of sample solid powder is weighed and dissolved in DMSO to prepare a mother liquor of 10^{-3} mol/L, dilute 1 mL of the above mother liquor 10 times to prepare a solution of 1×10^{-4} mol/L. Finally, the solution was mixed with water in different proportions to prepare a mixed solution with water contents of 0%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, and 90%, with a total volume of 3 mL, for fluorescence spectroscopy testing.

5. Cell Culture

4T1 cells (mouse breast cancer cell line) were obtained from National

Infrastructure of Cell Line Resource (NICR), and were cultured in RPMI-1640 media containing 10% FBS and 2% penicillin-streptomycin at 37 ℃ in a humidified atmosphere of 5% CO_2.

6. *In Vitro* Cytotoxicity

4T1 cells were seeded in 96-well plates at a density of 5 × 10^3 cells/well and incubated for 24 h. Then the cells were incubated with different concentrations of DHIPs in fresh medium. After further incubation for 24 h, the medium was removed and washed with PBS for three times. Cells were then incubated with fresh serum-free medium containing 10% MTT for 4 h in the dark. Then, all the media were removed and 150 μL DMSO was added. Finally, the absorbance of the products was measured at a wavelength of 570 nm by a microplate reader. The results were expressed as the viable percentage of cells after different treatments relative to the control cells without any treatment.

7. Colocalization Imaging in 4T1 Cell

4T1 cells were seeded in Φ20 mm glass bottom cell culture dishes (1.0 ± 0.05 × 10^6 cells in each dish). After overnight culture in a humidified incubator at 37 ℃ with 5% CO_2, culture medium was removed and cells were stained with cDHIPs (10 μM) for 15 min. After washed by PBS for 3 times, 4T1 cells were fixed with 4% fixative solution for 10 min. Before imaging, each dish was washed by PBS for 3 times. For co-localization with LysoTracker, the fixed cells were stained with LysoTracker (50 nM) for 10 min at 37 ℃.

8. Imaging of 3D Tumor Spheroid Model

Quickly add the heated agarose solution (dissolved in serum-free medium) to a 96 well low attachment culture plate and let it stand for at least 30 min for complete cooling. Then, inoculate 100 μL of tumor cells (1 × 10^4 cells mL^{-1}) into a 96-well low-attachment culture plate. After incubating in a 5% CO_2 humidified incubator at 37 ℃ for 72 h, its morphology can be observed. Then, the medium should be changed every 48 h or 72 h. After seven days of cultivation, the 3D tumor should be aspirated into Φ20 mm glass bottom cell culture dishes and treated with cDHIPs (10 μM) for 30 min. Before imaging, each dish was washed by PBS for 3 times.

9. Preparation of cDHIP-N-TPA-NPs

Dissolve 1mg cDHIP-N-TPA and 10mg Pluronic F127 in 1mL DMSO solution, and poured into 9 mL ultrapure water under ultrasonic conditions for 10 min. Centrifuge at 5000 rpm for 30 min using ultrafiltration centrifuge tubes to concentrate and obtain nanoparticles. It is named cDHIP-N-TPA-NPs. Ultrapure water was added to prepare a solution with a certain concentration for subsequent biological applications.

10. Animals

Animals: BALB/c (female, 5 weeks) mice were purchased from Chengdu Dashuo Experimental Animal Co., Ltd.

Statement of ethical approval: All mice were housed in designated animal facilities, fed ad libitum and inspected regularly. All animal studies were performed in accordance with the Regulations for Care and Use of Laboratory Animals and Guideline for Ethical Review animals (China, GB/T 35892-2018). All animal studies were approved by the Sichuan University Animal Charity Protection and Treatment Committee and performed in accordance with humane care and use of research animals. All animal procedures were reviewed and approved by Ethical Committees of West China School of Stomatology, Sichuan University (WCHSIRB-D-2017-042).

Feeding conditions: all the animals were submitted to controlled temperature conditions (22 ~ 26 ℃), humidity (50 ~ 60%) and light (12 h light/12 h dark, 15 ~ 20 LX).

11. Fluorescence imaging of tumors and major organs

BALB/c mice (female, 5 weeks, 18 in total) bearing 4T1 tumors (≈100 mm^3) were divided into 6 groups according to different circulation times: 3 h, 6 h, 9 h, 12 h, 24 h, and 48 h. cDHIP-N-TPA-NPs (10 μM,100 μL) were injected into different groups of mice by tail vein injection. The enrichment of Cdhip-N-TPA-NPs in heart, liver, spleen, lung, kidney and tumor were compared at 48 h. Fluorescence imaging of tumors and organs were captured by IVIS Lumina Series III.

12. Synthetic route

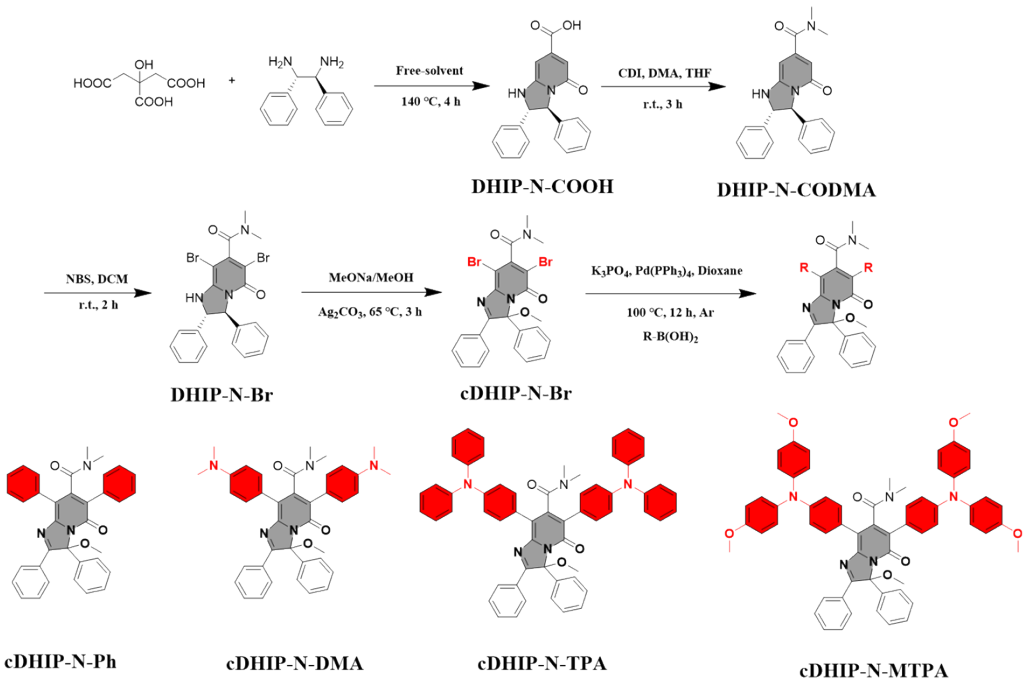


Fig. S1 The synthetic routes of target compounds.

Synthesis of compound DHIP-N-COOH： Add (1s, 2s) -1,2-diphenylethylenediamine (10.0 mmol, 2.1 g) and citric acid (10.0 mmol, 1.9 g) to the hydrothermal synthesis kettle. React at 140 ℃ for 4 h. After the reaction is completed, take out the crude product and place it in ethanol (40.0 mL). Heat it to 70 ℃, stir for

0.5 h, filter while hot, dry the filter cake, and obtain the final product with a yield of 87%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.29 (s, 1H), 8.42 (s, 1H), 7.47 – 7.37 (m, 5H), 7.37 – 7.31 (m, 3H), 7.27 – 7.20 (m, 2H), 6.01 (d, J = 1.5 Hz, 1H), 5.91 (d, J = 1.5 Hz, 1H), 5.32 (d, J = 2.7 Hz, 1H), 4.85 (d, J = 2.7 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 175.0, 171.8, 167.2, 160.1, 154.7, 145.2, 142.1, 139.9, 129.5, 129.3, 128.8, 128.5, 126.2, 126.1, 105.8, 80.8, 72.9, 68.1, 66.6, 43.2. HRMS(ESI): calcd for $C_{20}H_{17}N_2O_3^+$(M+H)$^+$: 333.1242, found: 333.1239.

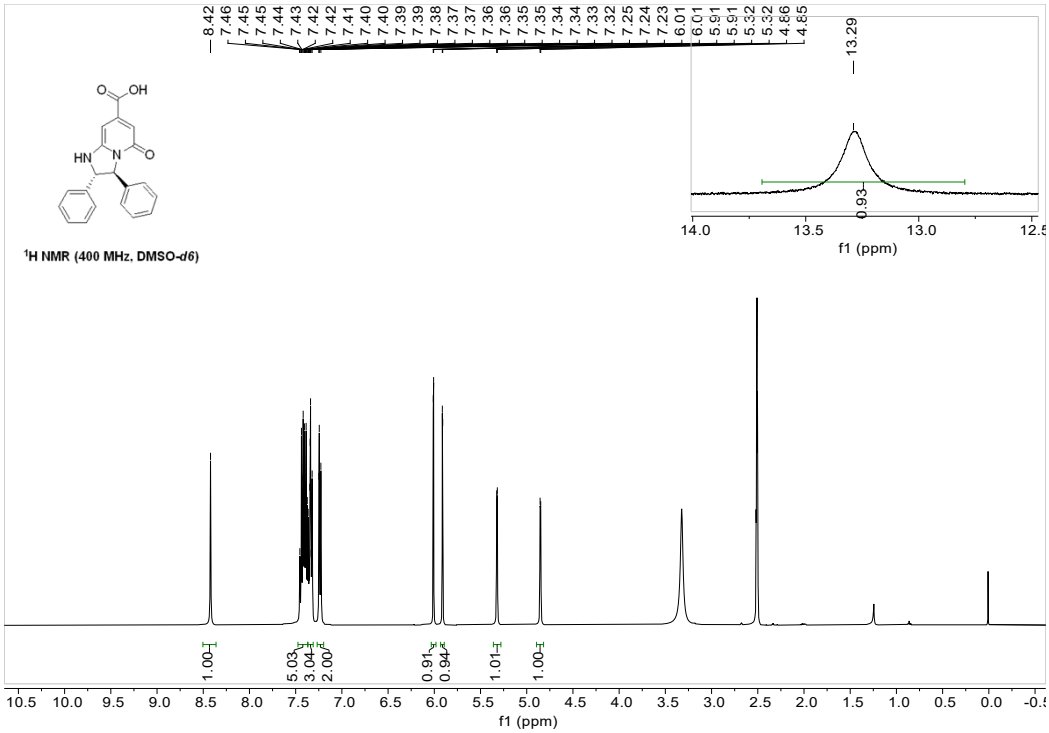


Fig. S2. ^{1}H NMR spectrum of compound DHIP-N-COOH in DMSO-*d6*.

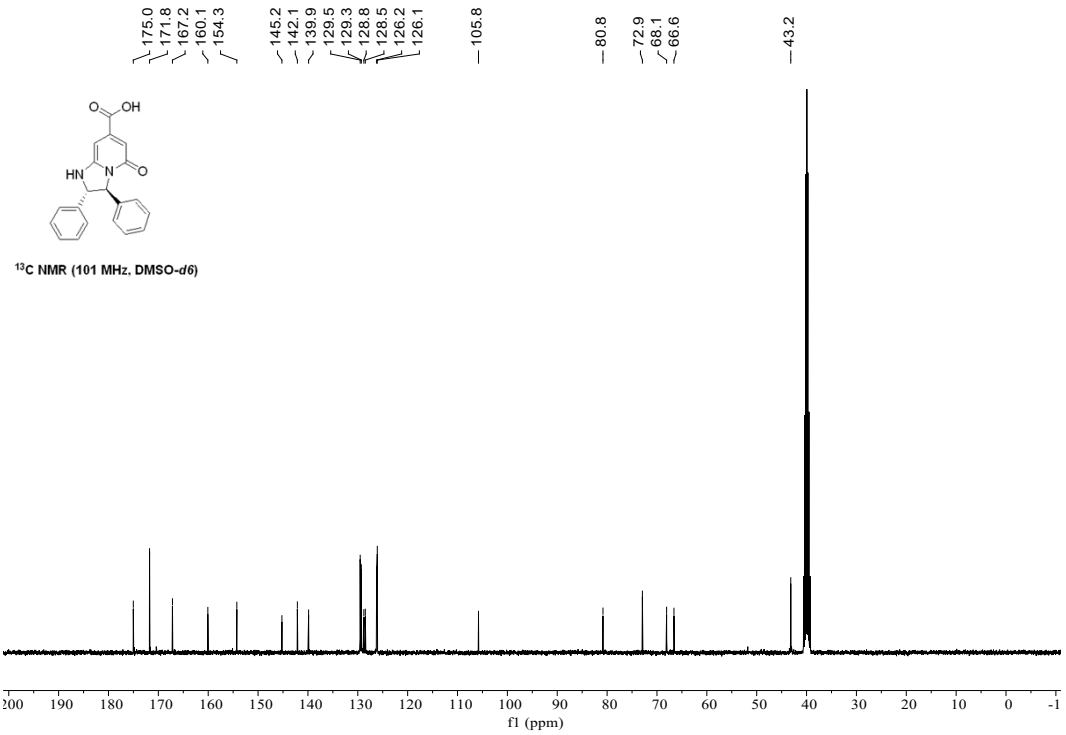


Fig. S3. ^{13}C NMR spectrum of compound DHIP-N-COOH in DMSO-*d6*.

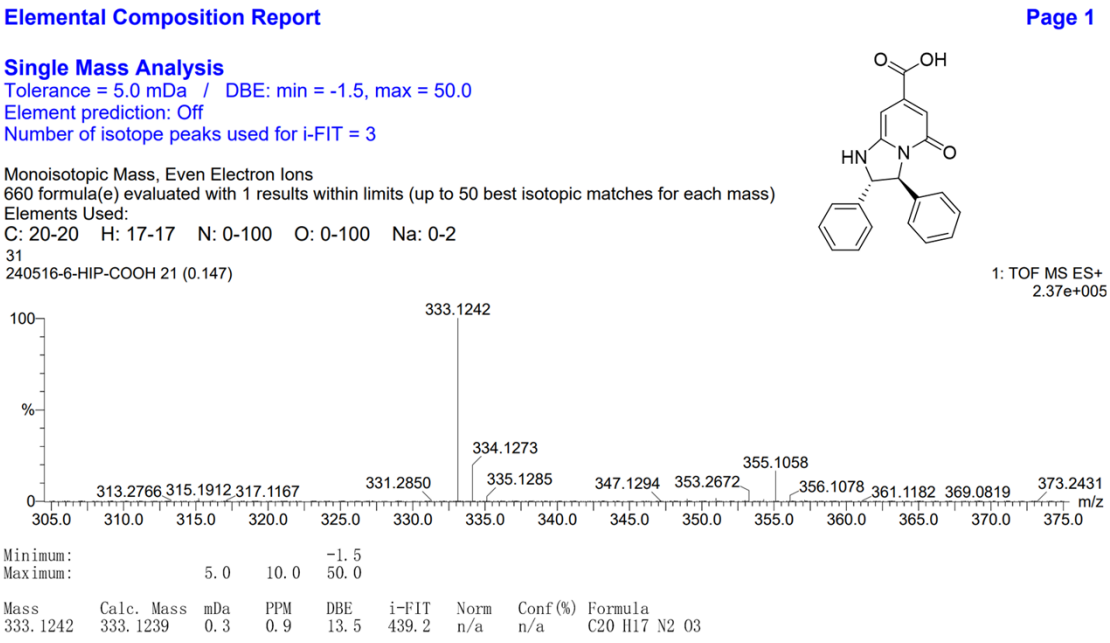


Fig. S4. HRMS spectrum of compound DHIP-N-COOH.

Synthesis of compound DHIP-N-CODMA: Place DHIP-N-COOH (2.0 mmol, 662.0 mg) in THF (15.0 mL), then add N, N '- carbonyl diimidazole (2.2 mmol, 356.7 mg) and stir for 1 h until the solution becomes clear and transparent. Slowly add dimethylamine (6.0 mmol, 3.0 mL) at 0 ℃ and continue the reaction at room temperature for 3 h. After that, the solution was extracted with dichloromethane and washed with water. Later the organic layer was dried over anhydrous $MgSO_4$. The

solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography using a dichloromethane/methanol mixture (100/1, V_{dcm}/V_m) as the eluent to give desired compound DHIP-N-CODMA with 84.7% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.39 (s, 1H), 7.46 – 7.32 (m, 8H), 7.24 (dd, J = 6.9, 1.7 Hz, 2H), 5.42 (d, J = 1.5 Hz, 1H), 5.39 (d, J = 1.4 Hz, 1H), 5.30 (d, J = 2.8 Hz, 1H), 4.81 (d, J = 2.8 Hz, 1H), 2.98 (s, 3H), 2.94 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.0, 159.8, 154.1, 151.6, 142.2, 140.1, 129.5, 129.3, 128.8, 128.4, 126.2, 126.1, 101.8, 79.8, 68.0, 66.5, 54.1, 49.1, 38.9, 34.6, 18.5, 17.2. **HRMS(ESI):** calcd for $C_{22}H_{22}N_3O_2^+(M+H)^+$: 360.1716, found: 360.1712.

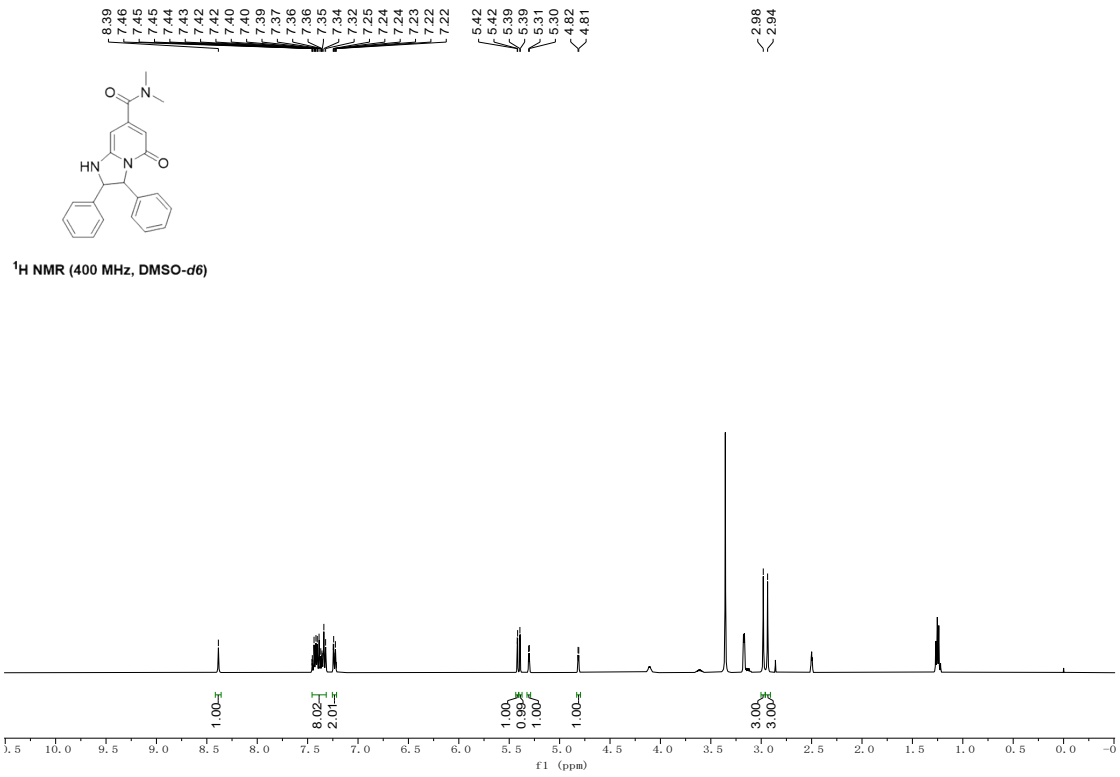


Fig. S5. ^{1}H NMR spectrum of compound DHIP-N-CODMA in DMSO-*d6*.

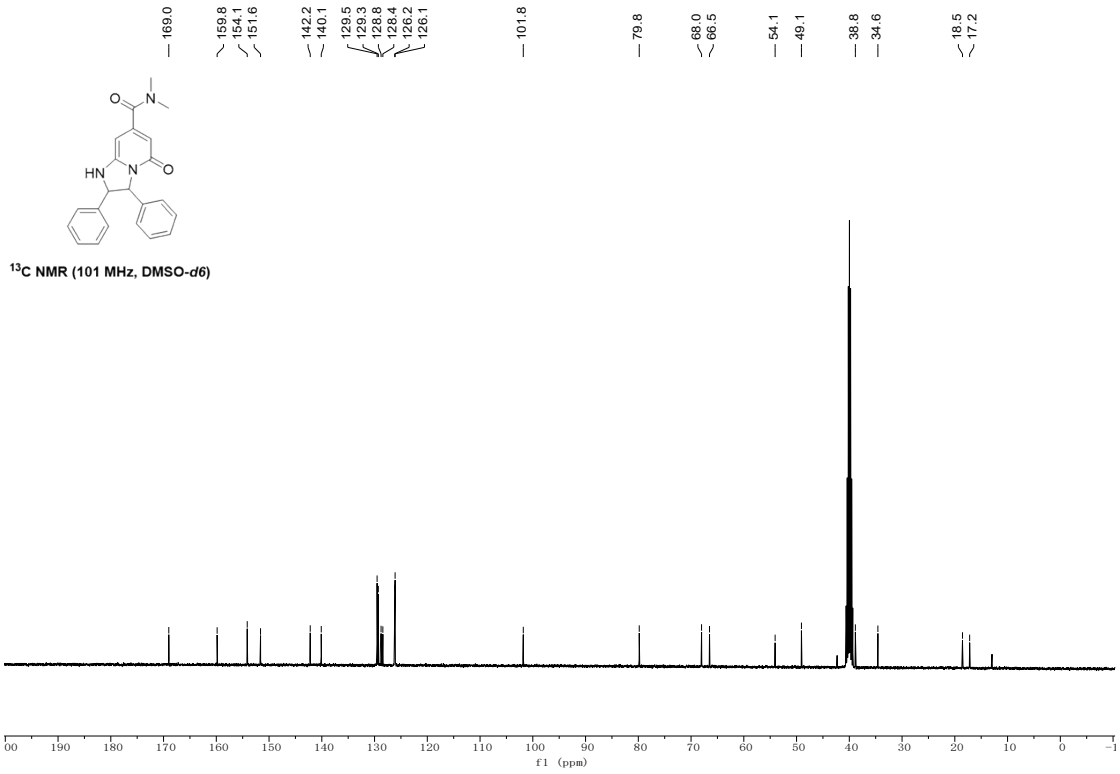


Fig. S6. ^{13}C NMR spectrum of compound DHIP-N-CODMA in DMSO-*d6*.

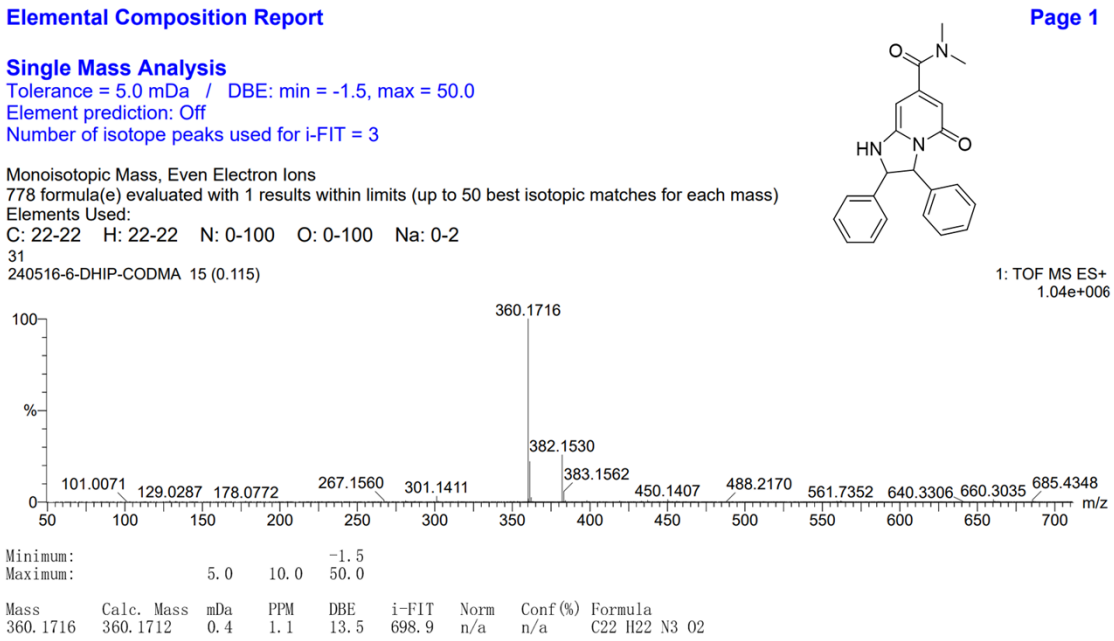


Fig. S7. HRMS spectrum of compound DHIP-N-CODMA.

Synthesis of compound DHIP-N-Br: Dissolve compound DHIP-N-CODMA (2.0 mmol, 718.0 mg) in dichloromethane (30.0 mL), then add N-bromosuccinimide (6.0 mmol, 1.1 g) and react at room temperature for 1 h. After that, the solution was extracted with dichloromethane and washed with water. Later the organic layer was dried over

anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography using an ethyl acetate/petroleum ether mixture (1/10, V_{ea}/V_p) as the eluent to give desired compound DHIP-N-Br with 88.2% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.85 (d, J = 10.4 Hz, 1H), 7.44 – 7.31 (m, 8H), 7.25 (t, J = 7.5 Hz, 2H), 5.42 (dd, J = 15.9, 4.1 Hz, 1H), 4.89 (t, J = 4.3 Hz, 1H), 2.99 (d, J = 2.4 Hz, 3H), 2.94 (d, J = 3.3 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.5, 155.1, 151.1, 151.1, 141.2, 139.4, 129.5, 129.5, 129.0, 128.8, 126.6, 126.4, 94.1, 70.8, 68.7, 67.0, 55.4, 37.2, 34.1. HRMS(ESI): calcd for $C_{22}H_{20}N_3O_2Br_2^+(M+H)^+$: 515.9918, found: 515.9922.

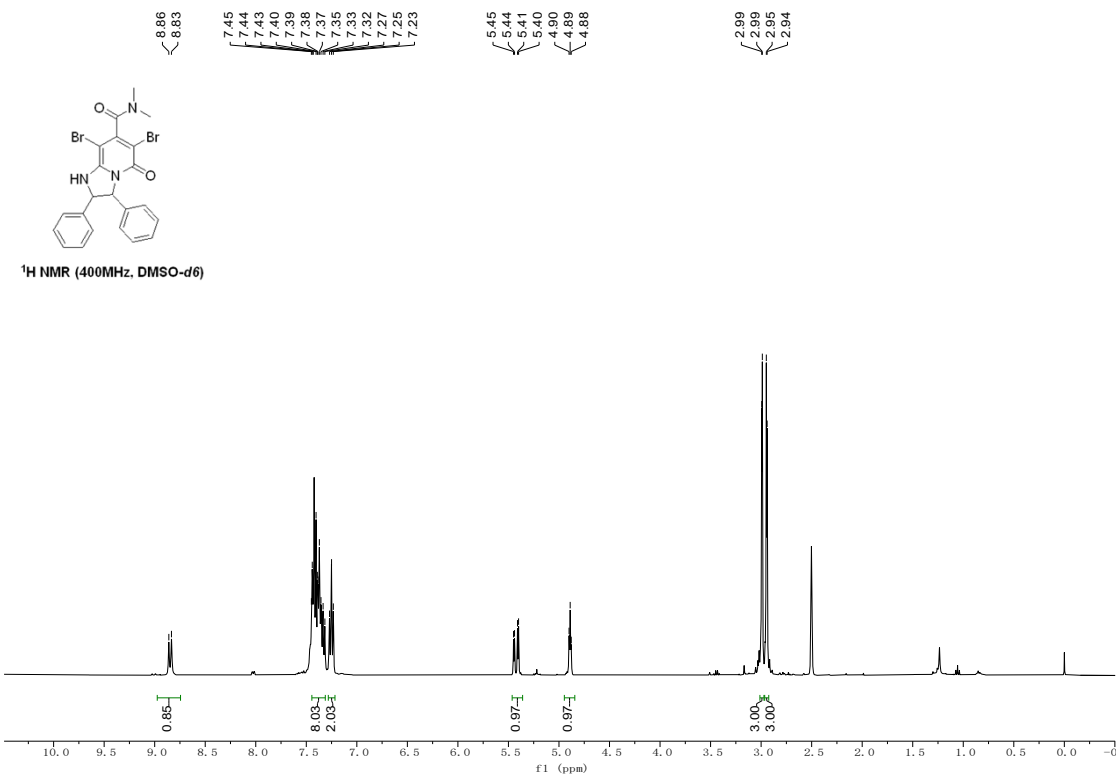


Fig. S8. ^{1}H NMR spectrum of compound DHIP-N-Br in DMSO-*d6*.

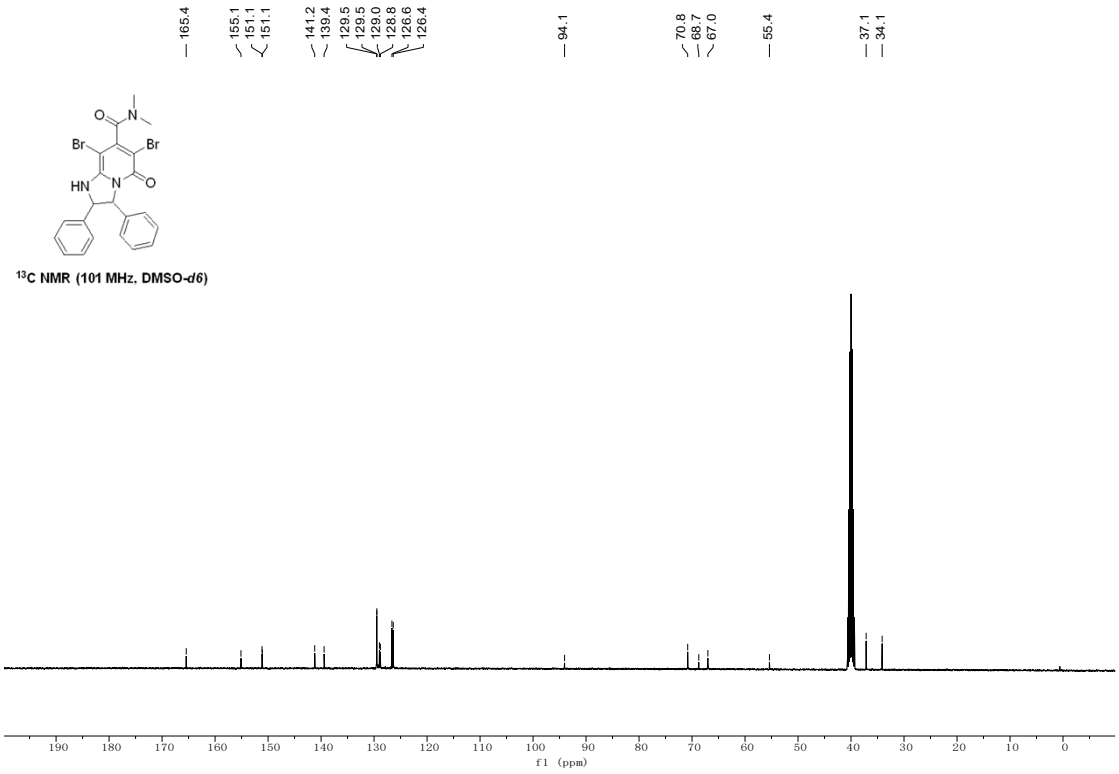


Fig. S9. ^{13}C NMR spectrum of compound DHIP-N-Br in DMSO-*d6*.

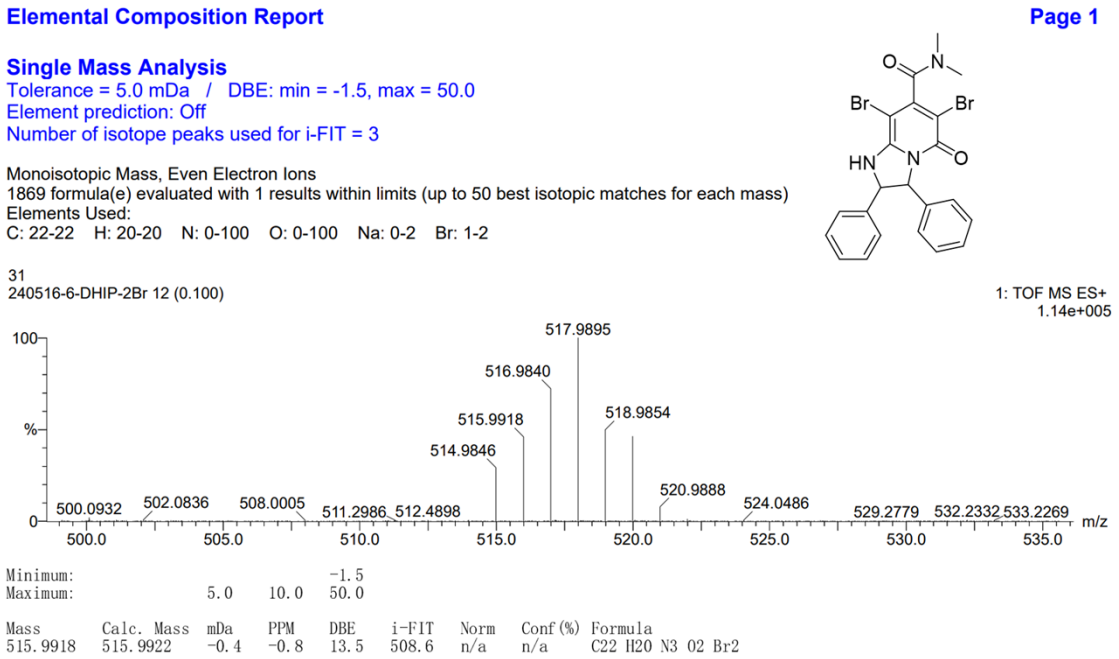


Fig. S10. HRMS spectrum of compound DHIP-N-Br.

Synthesis of compound cDHIP-N-Br: Dissolve compound DHIP-N-Br (2.0 mmol, 1.0 g) in methanol (30.0 mL), add silver carbonate (2.0 mmol, 551.5 mg) and sodium

methoxide (8.0 mmol, 432.0 mg), and react at 65 ℃ for 3 h. Adjust the pH of the reaction mixture to 3-4 and filter to remove the filter residue. After that, the solution was extracted with dichloromethane and washed with water. Later the organic layer was dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography using an ethyl acetate/petroleum ether mixture (1/8, V_{ea}/V_p) as the eluent to give desired compound cDHIP-N-Br with 8.2% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 7.1 Hz, 2H), 7.53 (dd, *J* = 7.5, 2.4 Hz, 3H), 7.42 – 7.33 (m, 5H), 3.33 (s, 3H), 3.19 (s, 3H), 3.03 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.2, 165.2, 154.1, 151.5, 150.1, 134.2, 133.1, 129.9, 129.8, 129.2, 128.9, 128.7, 126.3, 114.0, 105.8, 89.7, 52.7, 37.3, 34.6, 29.8. HRMS(ESI): calcd for $C_{23}H_{19}N_3O_3Br_2Na^+$(M+Na)$^+$: 565.9696, found: 565.9691.

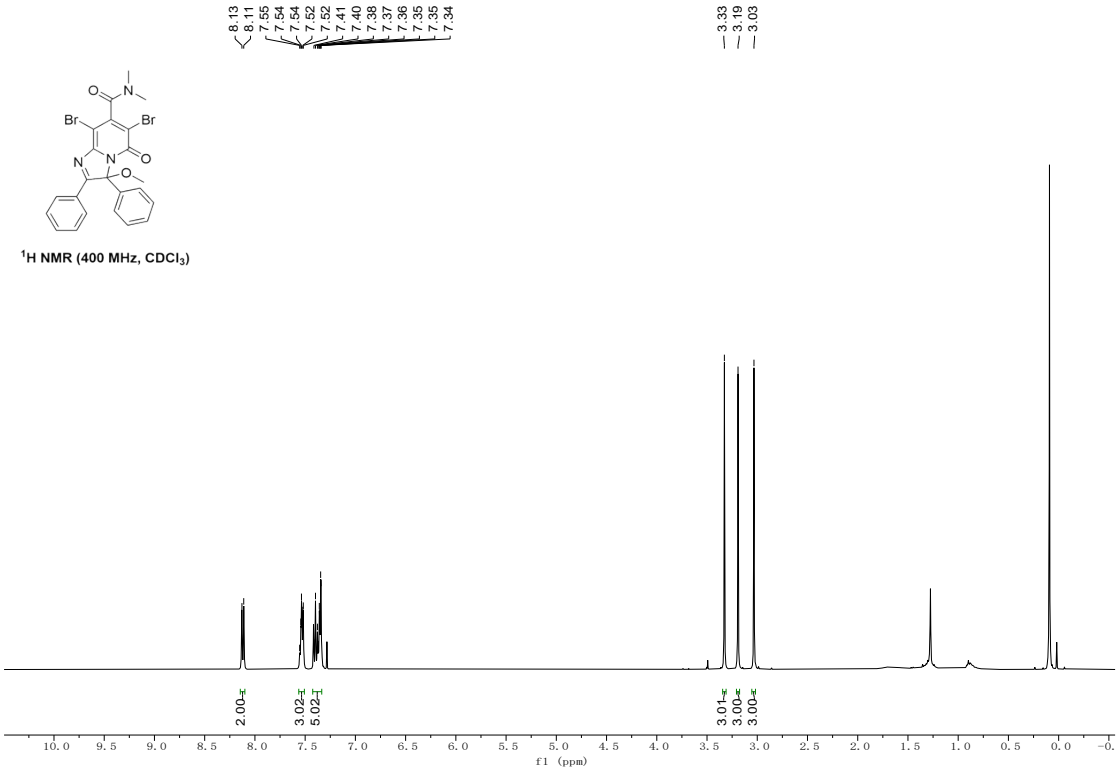


Fig. S11. ^{1}H NMR spectrum of compound cDHIP-N-Br in Chloroform-*d*.

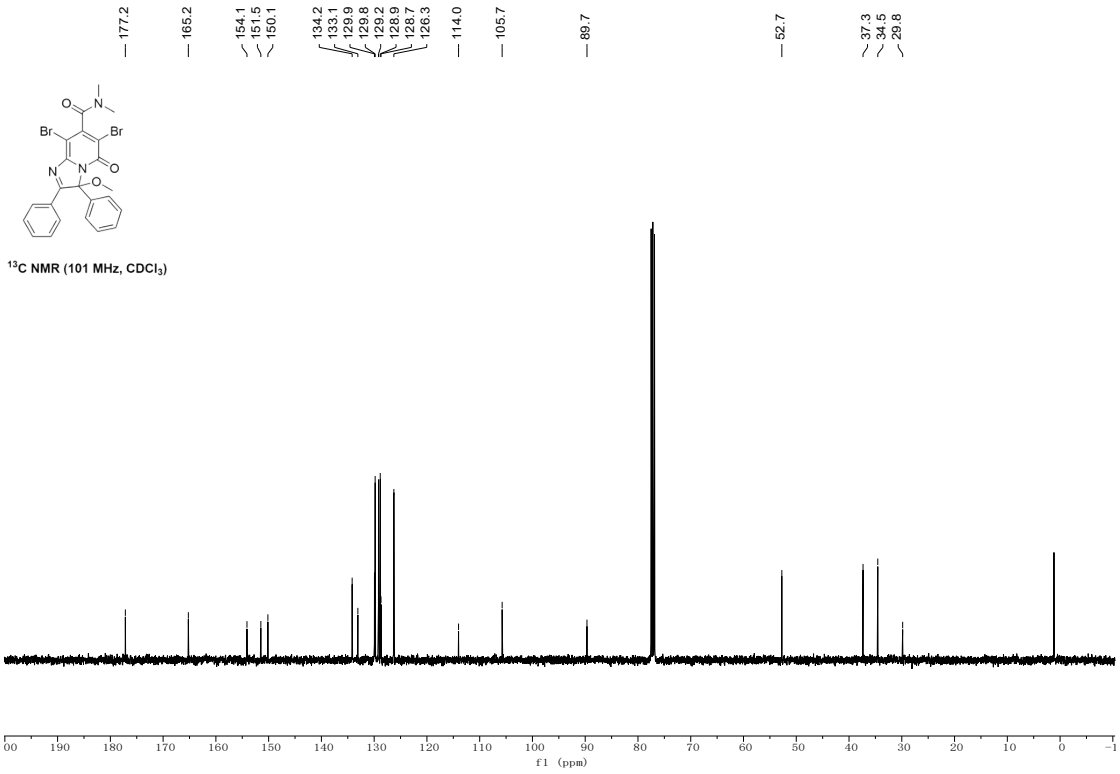


Fig. S12. ^{13}C NMR spectrum of compound cDHIP-N-Br in Chloroform-*d*.

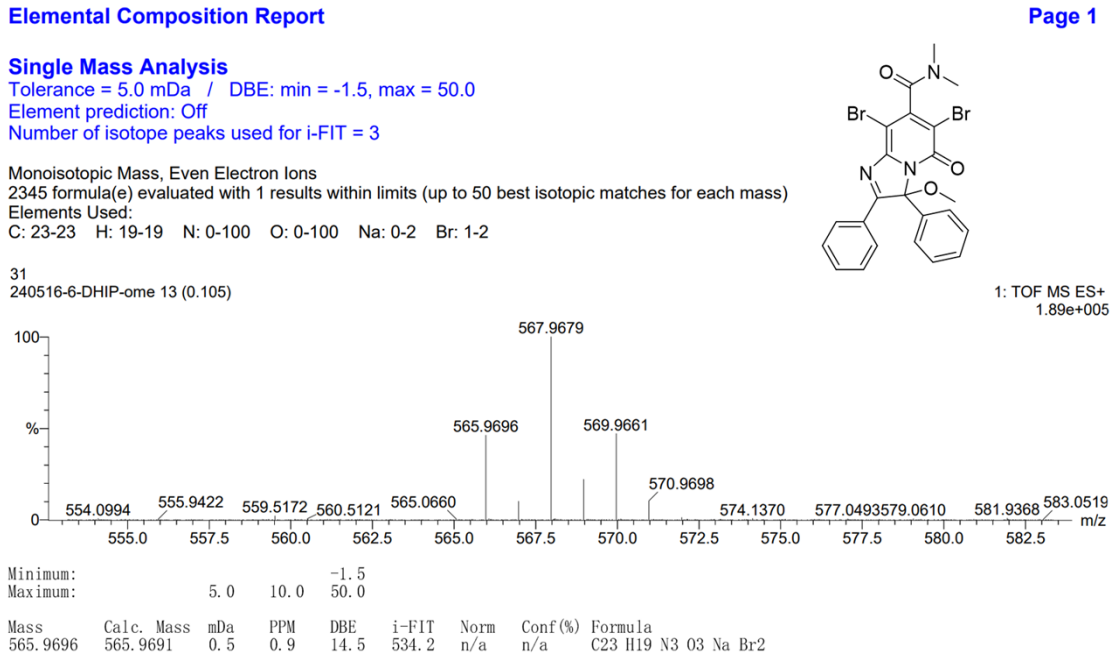


Fig. S13. HRMS spectrum of compound cDHIP-N-Br.

Synthesis of compound cDHIP-N-Ph: Dissolve compound cDHIP-N-Br (0.2 mmol, 109.0 mg) in 1,4-dioxane (15.0 mL), add potassium phosphate (0.6 mmol, 127.2 mg), tetratriphenylphosphine palladium (0.02 mmol, 23.1 mg), and phenylboronic acid (1.0 mmol, 122.0 mg), and react for 12 h under argon protection at 100 ℃. After that, the

solution was extracted with ethyl acetate and washed with water. Later the organic layer was dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography using an ethyl acetate/petroleum ether mixture (1/10, V_{ea}/V_p) as the eluent to give desired cDHIP-N-Ph with 29.0% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 7.3 Hz, 2H), 7.58 – 7.51 (m, 4H), 7.49 – 7.35 (m, 8H), 7.30 (dd, *J* = 10.9, 7.7 Hz, 6H), 3.40 (s, 3H), 2.63 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.9, 165.7, 156.8, 149.8, 146.2 133.1, 132.2, 132.2, 131.9, 129.4, 128.9, 128.3, 128.2, 128.1, 127.7, 127.5, 127.1, 127.0, 126.7, 125.1, 111.7, 102.1, 51.2, 36.6, 32.8. HRMS(ESI): calcd for $C_{35}H_{29}N_3O_3Na^+$(M+Na)$^+$: 562.2111, found: 562.2107.

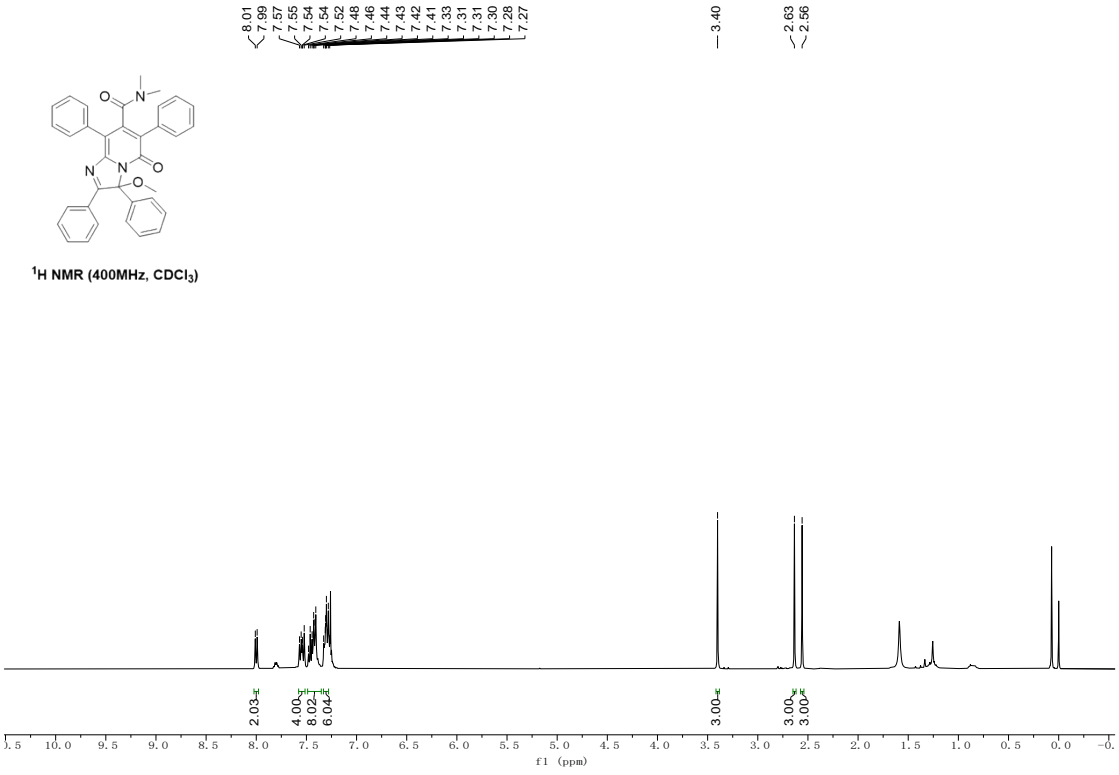
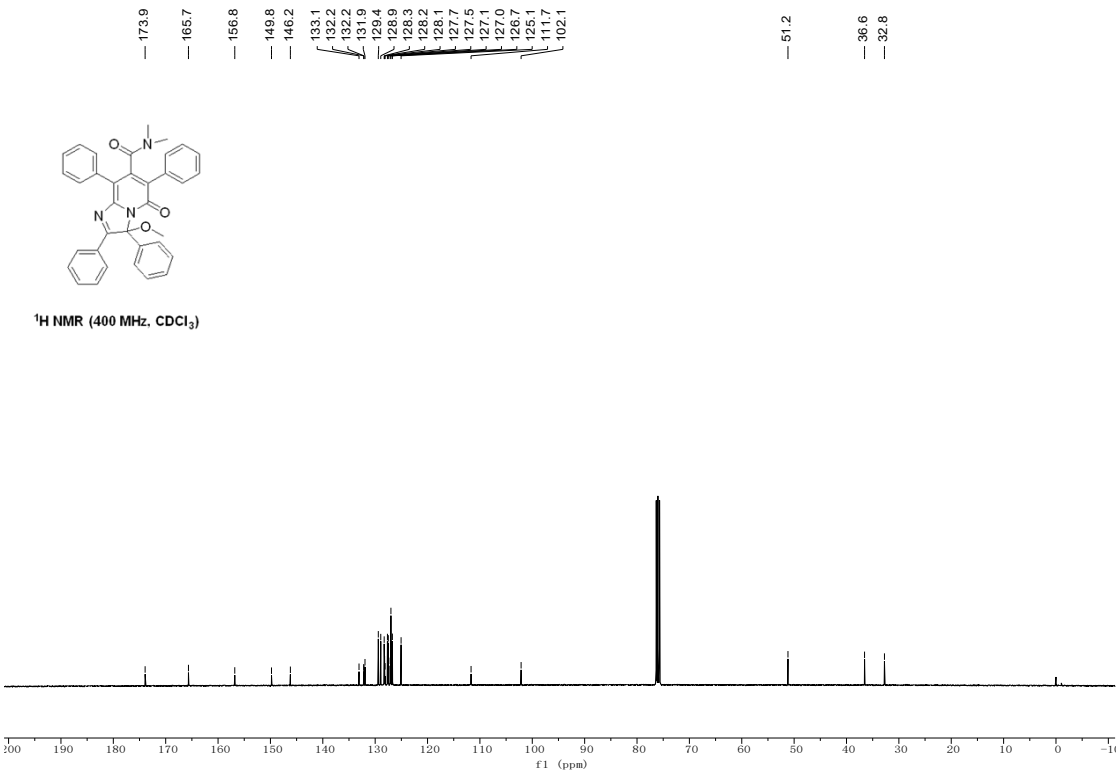


Fig. S14. ^{1}H NMR spectrum of cDHIP-N-Ph in Chloroform-*d*.



^{1}H NMR (400 MHz, $CDCl_3$)

Fig. S15. ^{13}C NMR spectrum of cDHIP-N-Ph in Chloroform-*d*.

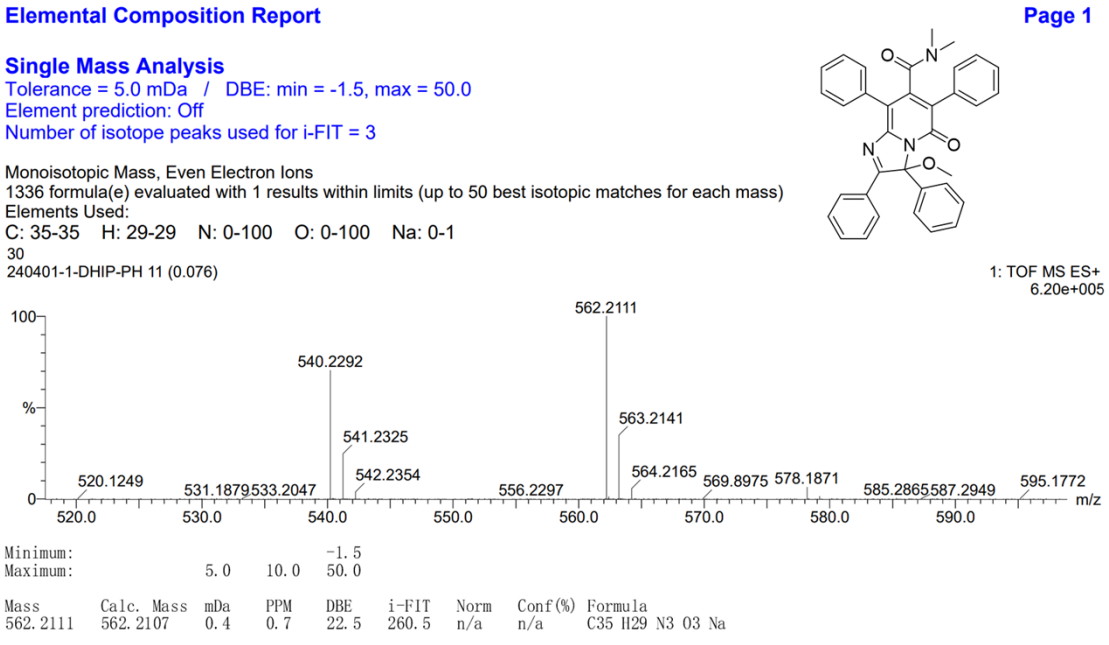


Fig. S16. HRMS spectrum of cDHIP-N-Ph.

Synthesis of compound cDHIP-N-DMA: Dissolve compound cDHIP-N-Br (0.2 mmol, 109.0 mg) in 1,4-dioxane (15.0 mL), add potassium phosphate (0.6 mmol, 127.2 mg), tetratriphenylphosphine palladium (0.02 mmol, 23.1 mg), and 4-(Dimethylamino) phenylboronic acid (1.0 mmol, 165.0 mg), and react for 12 h under argon protection at

100 ℃. After that, the solution was extracted with ethyl acetate and washed with water. Later the organic layer was dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography using an ethyl acetate/petroleum ether mixture (1/10, V_{ea}/V_p) as the eluent to give desired cDHIP-N-DMA with 26.0% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 – 7.98 (m, 2H), 7.58 – 7.53 (m, 2H), 7.43 – 7.34 (m, 4H), 7.33 – 7.27 (m, 4H), 7.26 – 7.18 (m, 2H), 6.82 – 6.77 (m, 2H), 6.66 – 6.62 (m, 2H), 3.37 (s, 3H), 3.02 (s, 6H), 2.91 (s, 6H), 2.66 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.9, 166.7, 157.2, 149.2, 148.9, 148.6, 144.9, 133.5, 131.3, 130.1, 129.9, 128.5, 128.1, 128.0, 127.9, 127.5, 127.3, 125.2, 120.2, 120.0, 112.4, 110.8, 110.7, 101.8, 51.0, 39.4, 36.6, 33.0. HRMS(ESI): calcd for $C_{39}H_{40}N_5O_3^+$(M+H)$^+$: 626.3128, found: 626.3131.

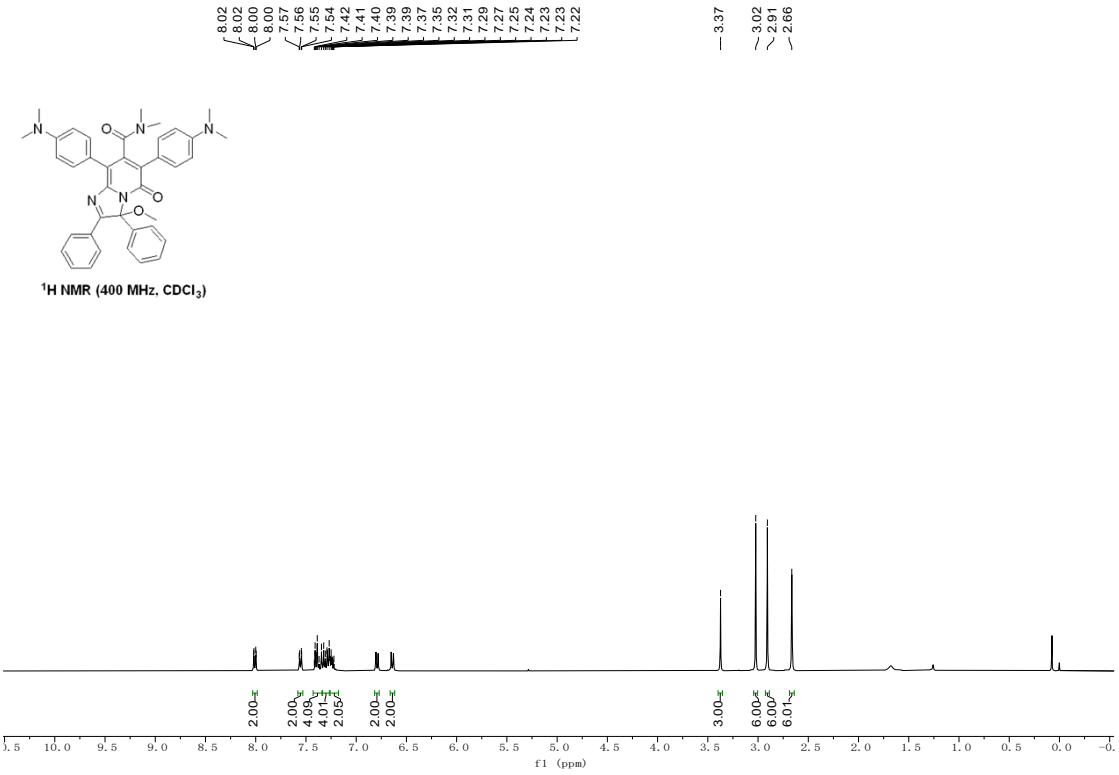


Fig. S17. ^{1}H NMR spectrum of cDHIP-N-DMA in Chloroform-*d*.

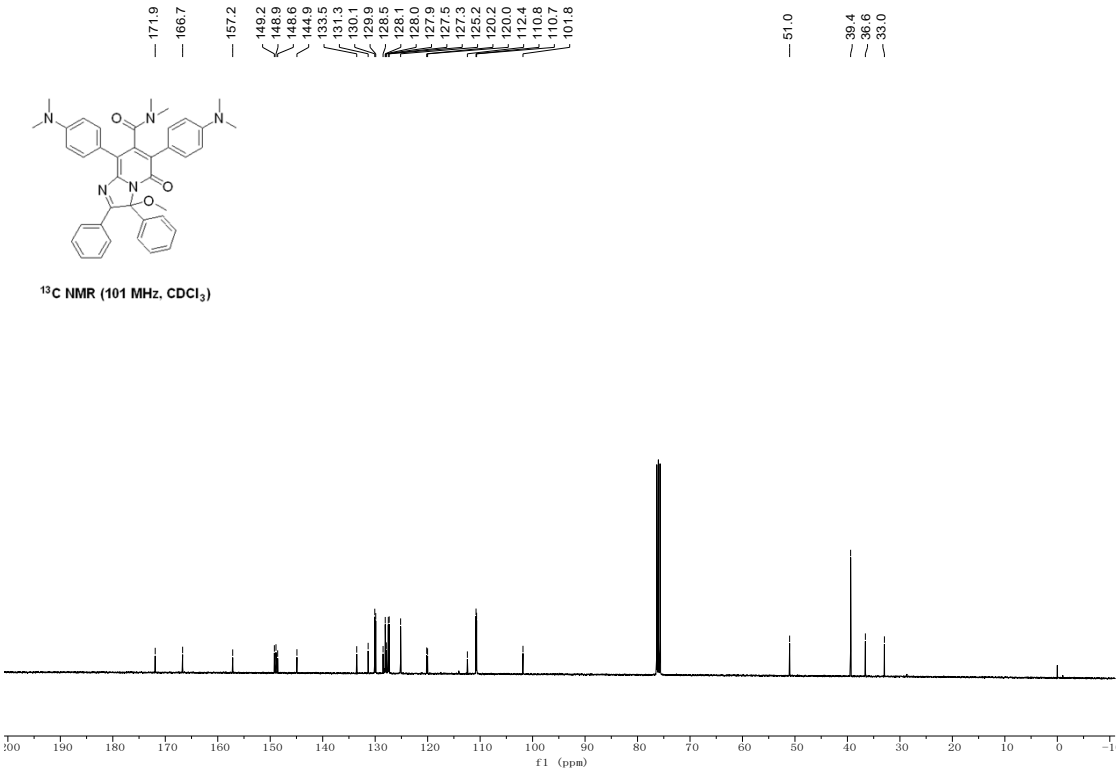


Fig. S18. ^{13}C NMR spectrum of cDHIP-N-DMA in Chloroform-*d*.

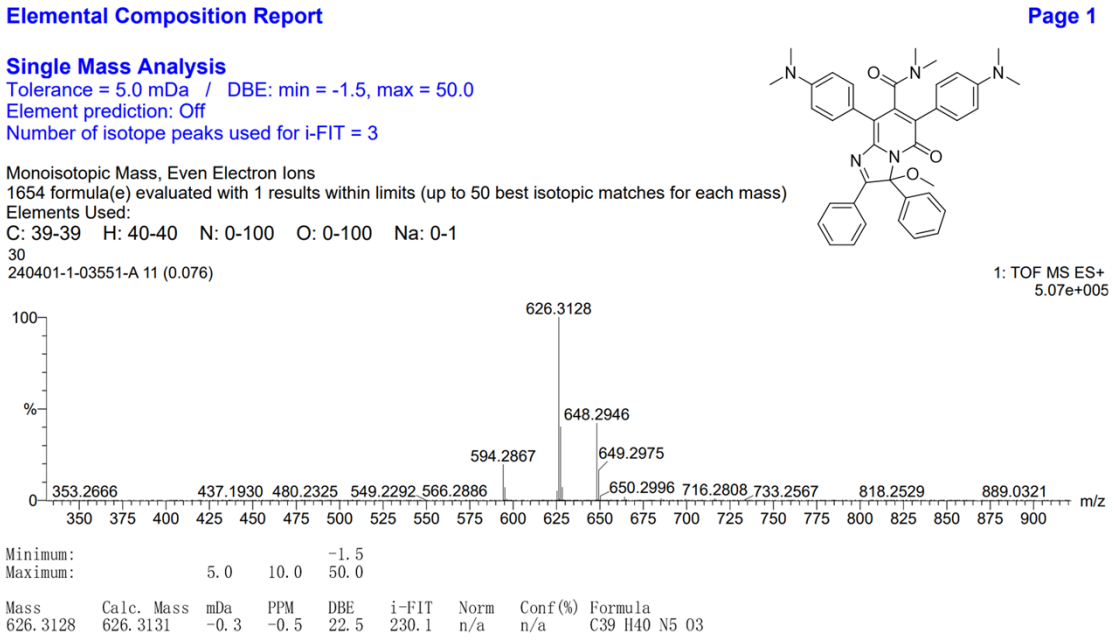


Fig. S19. HRMS spectrum of cDHIP-N-DMA.

Synthesis of compound cDHIP-N-TPA: Dissolve compound cDHIP-N-Br (0.2 mmol, 109.0 mg) in 1,4-dioxane (15.0 mL), add potassium phosphate (0.6 mmol, 127.2 mg), tetratriphenylphosphine palladium (0.02 mmol, 23.1 mg), and 4-(Diphenylamino) phenylboronic acid (1.0 mmol, 289.0 mg), and react for 12 h under argon protection at

100 ℃. After that, the solution was extracted with ethyl acetate and washed with water. Later the organic layer was dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography using an ethyl acetate/petroleum ether mixture (1/10, V_{ea}/V_p) as the eluent to give desired cDHIP-N-TPA with 25.0% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 8.02 (m, 2H), 7.62 – 7.57 (m, 2H), 7.48 – 7.36 (m, 4H), 7.36 – 7.30 (m, 10H), 7.27 – 7.21 (m, 8H), 7.17 – 7.14 (m, 2H), 7.08 (d, *J* = 7.8 Hz, 6H), 7.05 – 6.99 (m, 4H), 3.40 (s, 3H), 2.72 (s, 3H), 2.71 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.3, 150.3, 147.6, 147.6, 147.5, 147.5, 146.8, 134.3, 132.8, 131.2, 130.9, 129.3, 129.2, 128.7, 128.6, 128.5, 127.1, 126.6, 126.1, 125.0, 124.6, 123.3, 123.1, 122.3, 122.0, 112.7, 103.1, 52.1, 37.7, 33.9, 29.7. HRMS(ESI): calcd for $C_{59}H_{48}N_5O_3^+(M+H)^+$: 874.3760, found: 874.3757.

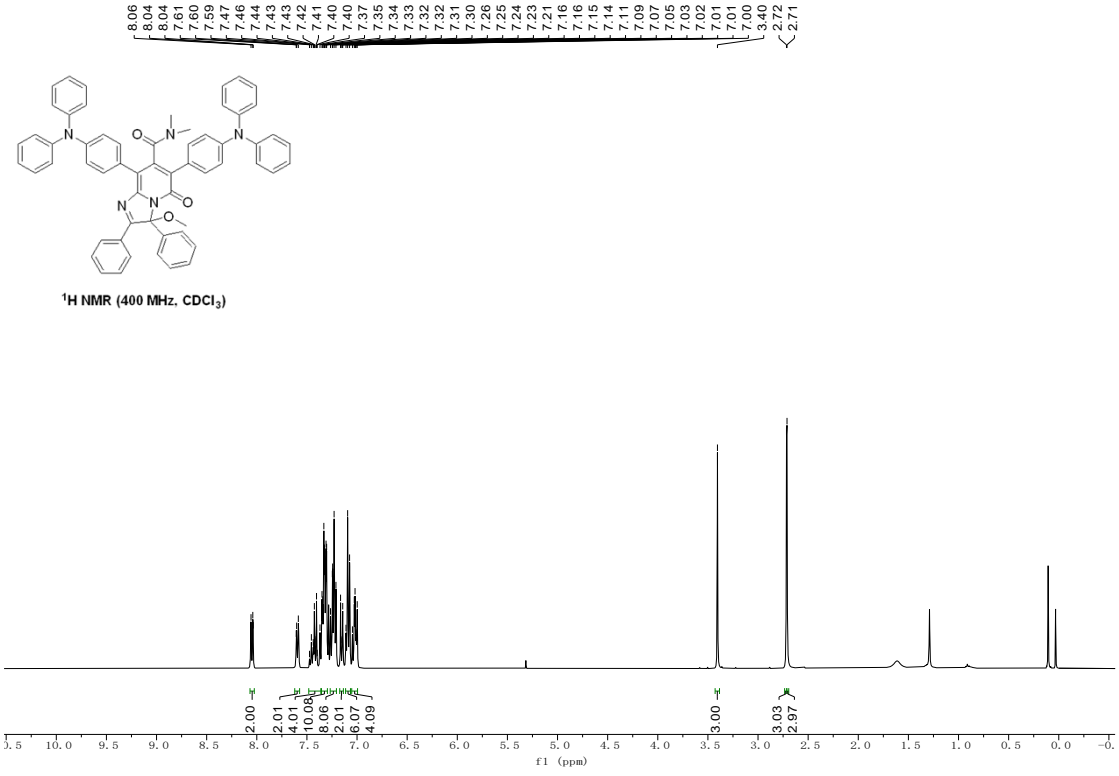


Fig. S20. ^{1}H NMR spectrum of cDHIP-N-TPA in Chloroform-*d*.

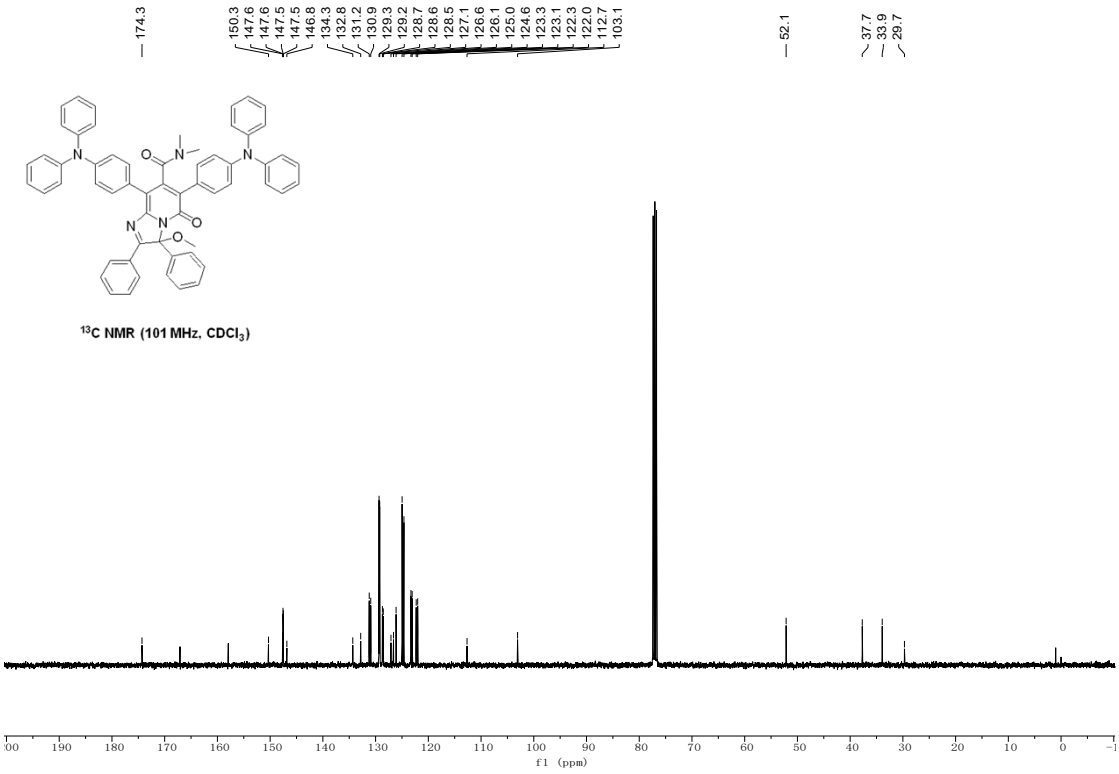


Fig. S21. ^{13}C NMR spectrum of cDHIP-N-TPA in Chloroform-*d*.

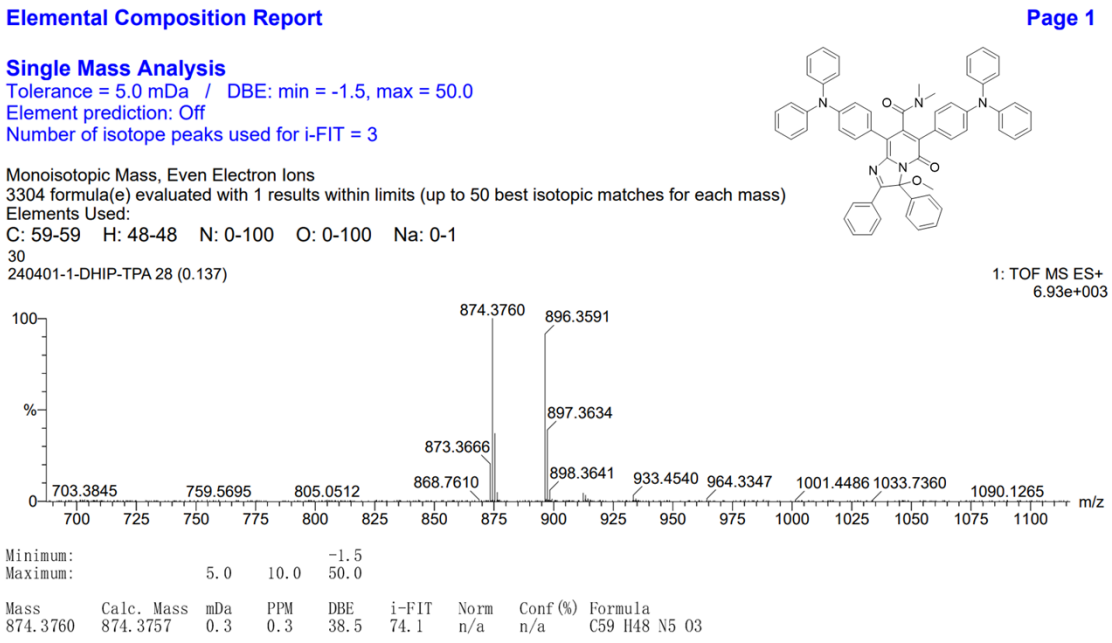


Fig. S22. HRMS spectrum of cDHIP-N-TPA.

Synthesis of compound cDHIP-N-MTPA: Dissolve compound cDHIP-N-Br (0.2 mmol, 109.0 mg) in 1,4-dioxane (15.0 mL), add potassium phosphate (0.6 mmol, 127.2 mg), tetratriphenylphosphine palladium (0.02 mmol, 23.1 mg), and (4-(Bis(4-methoxyphenyl)amino)phenyl)boronic acid (1.0 mmol, 349.2 mg), and react for 12 h

under argon protection at 100 ℃. After that, the solution was extracted with ethyl acetate and washed with water. Later the organic layer was dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography using an ethyl acetate/petroleum ether mixture (1/10, V_{ea}/V_p) as the eluent to give desired cDHIP-N-MTPA with 24.0% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 7.1 Hz, 2H), 7.48 (d, *J* = 6.7 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.25 – 7.17 (m, 7H), 7.16 – 7.13 (m, 2H), 7.10 – 7.06 (m, 4H), 6.96 – 6.92 (m, 4H), 6.91 – 6.87 (m, 2H), 6.82 – 6.77 (m, 4H), 6.77 – 6.74 (m, 2H), 6.73 – 6.69 (m, 4H), 3.74 (s, 6H), 3.71 (s, 6H), 3.29 (s, 3H), 2.61 (s, 3H), 2.60 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.7, 166.3, 157.0, 155.1, 154.9, 148.9, 147.4, 147.3, 145.3, 139.6, 139.6, 133.3, 131.6, 129.9, 129.7, 128.3, 128.1, 128.1, 127.8, 127.6, 127.5, 126.2, 125.7, 125.1, 123.9, 123.4, 118.1, 117.7, 113.7, 113.6, 112.0, 101.9, 54.5, 54.5, 51.1, 36.7, 33.0. HRMS(ESI): calcd for $C_{63}H_{55}N_5O_7Na^+$(M+Na)$^+$: 1016.4005, found: 1016.3999.

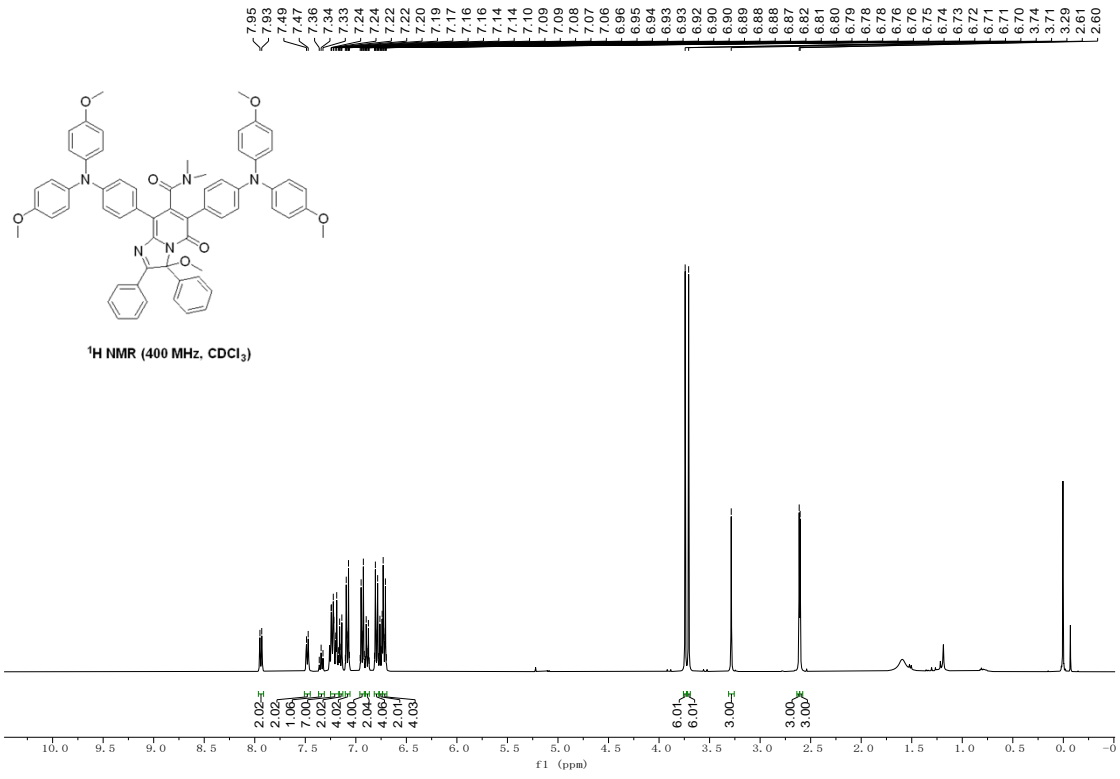


Fig. S23. ^{1}H NMR spectrum of cDHIP-N-MTPA in Chloroform-*d*.

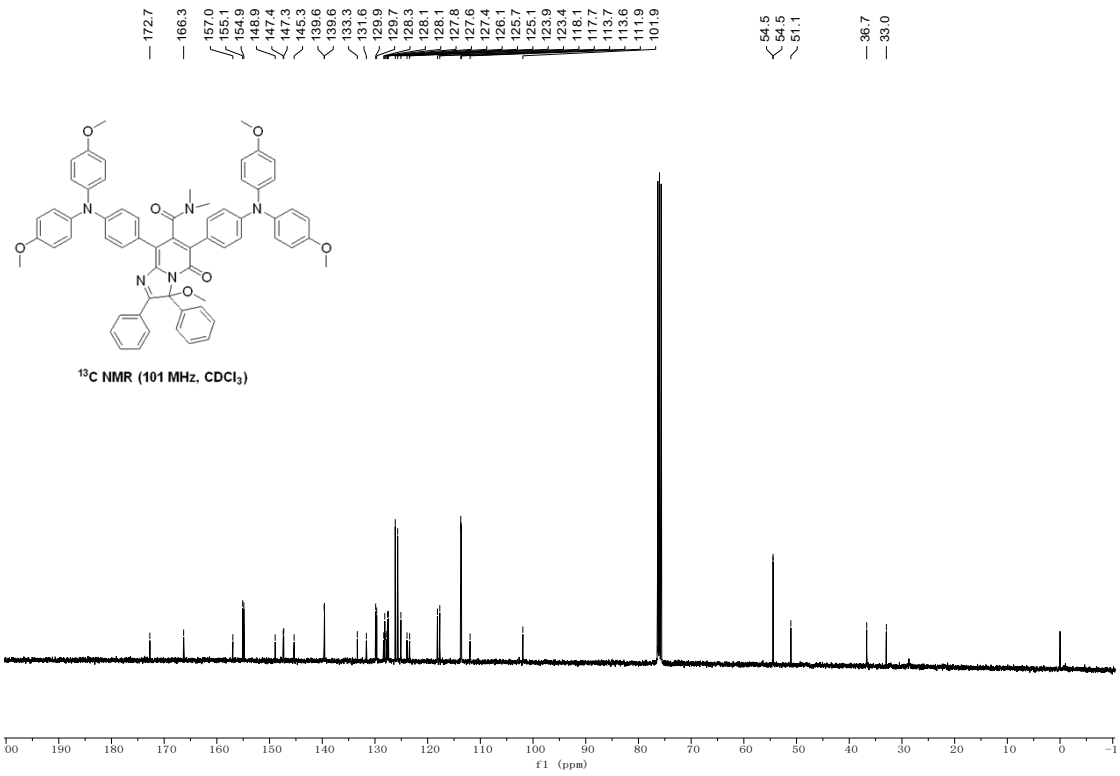


Fig. S24. ^{13}C NMR spectrum of cDHIP-N-MTPA in Chloroform-*d*.

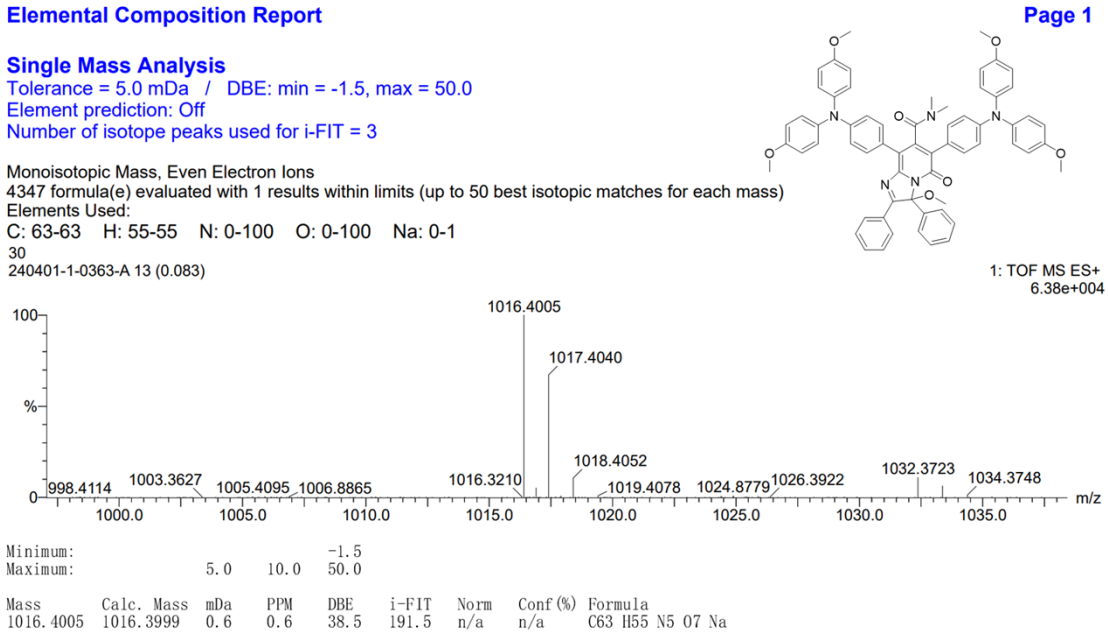


Fig. S25. HRMS spectrum of cDHIP-N-MTPA.

13. Photophysical properties

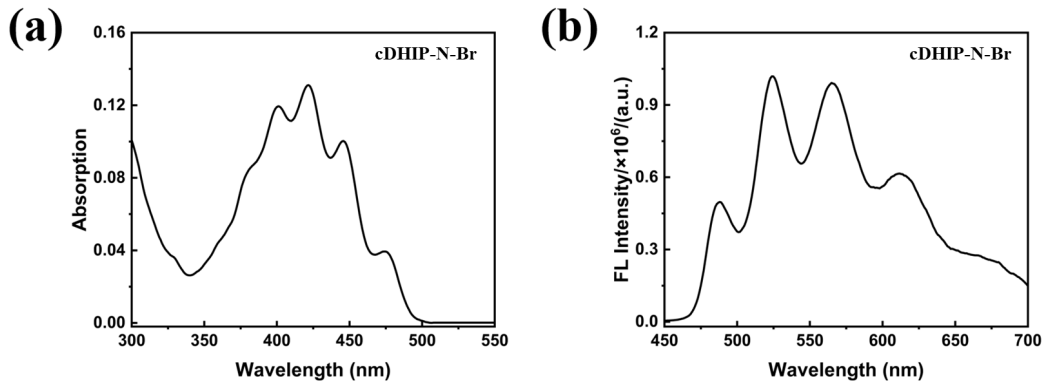


Fig. S26. (a) UV absorption spectra of cDHIP-N-Br and (b) FL spectra of cDHIP-N-Br. [cDHIP-N-Br] = 10 μM. (λ_{ex} = 422 nm)

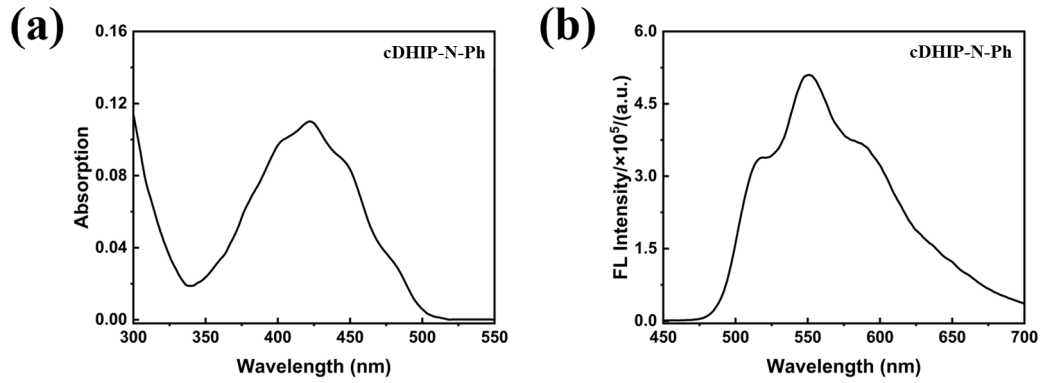


Fig. S27. (a) UV absorption spectra and (b) FL spectra of cDHIP-N-Ph. [cDHIP-N-Ph] = 10 μM. (λ_{ex} = 423 nm)

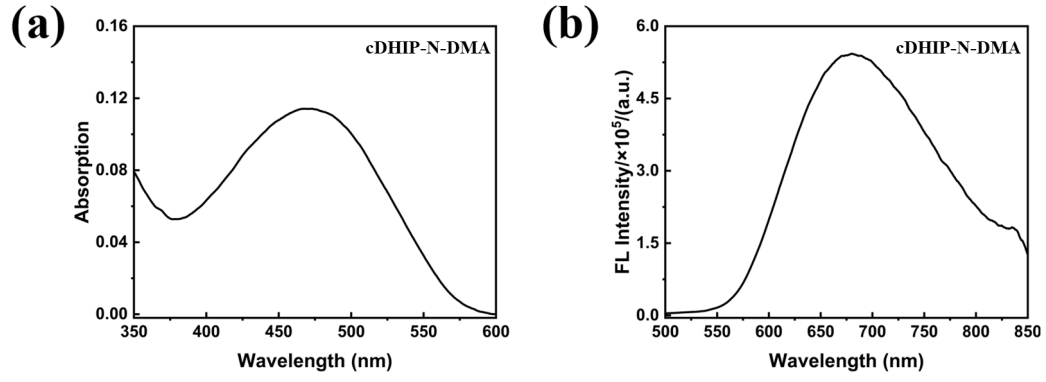


Fig. S28. (a) UV absorption spectra and (b) FL spectra of cDHIP-N-DMA. [cDHIP-N-DMA] = 10 μM. (λ_{ex} = 470 nm)

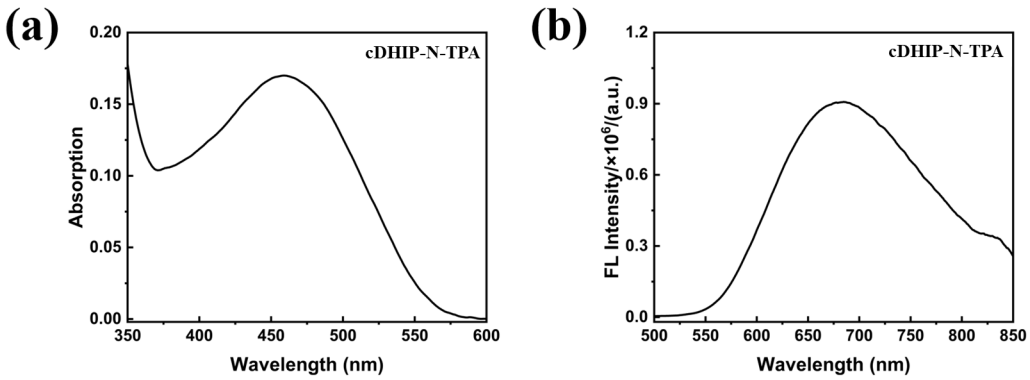


Fig. S29. (a) UV absorption spectra and (b) FL spectra of cDHIP-N-TPA. [cDHIP-N-TPA] = 10 μM. (λ_{ex} = 455 nm)

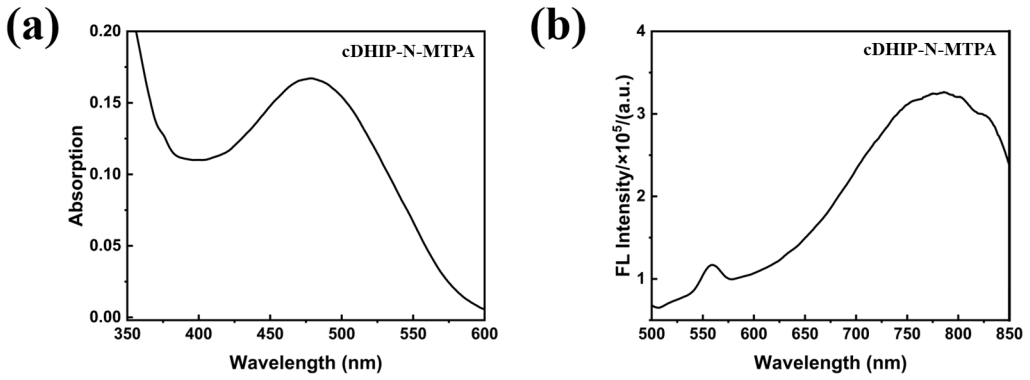


Fig. S30. (a) UV absorption spectra and (b) FL spectra of cDHIP-N-MTPA. [cDHIP-N-MTPA] = 10 μM. (λ_{ex} = 475 nm)

Table S1. Photophysical Properties of cDHIPs derivatives

Compounds	λ_{abs} [a] (nm)	ε[b] (M^{-1} cm^{-1})	λ_{em} [a] (nm)	Stokes shift [a]	Φ[c] (%)	λ_{em} range (nm)
cDHIP-N-Br	422	1.21×10^4	535	113	73.44	470-700 (VIS)
cDHIP-N-Ph	423	1.13×10^4	550	127	74.35	480-700 (VIS)
cDHIP-N-DMA	470	1.40×10^4	680	210	3.89	550-850 (NIR I)
cDHIP-N-TPA	455	1.59×10^4	685	230	3.03	550-850 (NIR I)
cDHIP-N-MTPA	475	1.61×10^4	795	320	3.30	550-850 (NIR I)

[a] the wavelength corresponds to the maximum Stokes shift in different solvents, [b] maximum λ_{abs} in DMSO, [c] maximum λ_{em} in DMSO

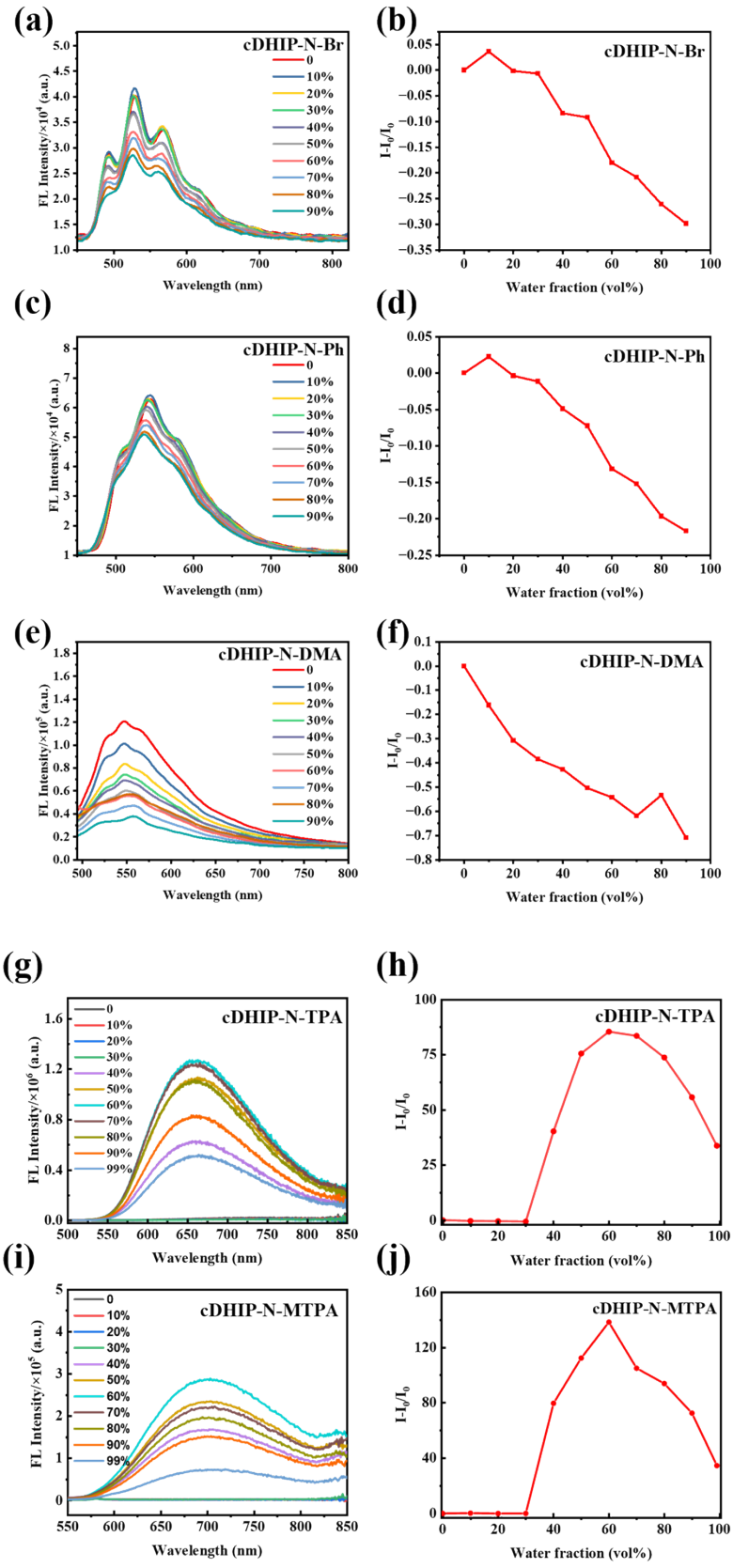


Fig. S31. FL spectra of (a) cDHIP-N-Br (c) cDHIP-N-Ph (e) cDHIP-N-DMA (g) cDHIP-N-TPA (i) cDHIP-N-MTPA in DMSO/water mixtures. Correlation between the net change in FL intensity [$(I-I_0)/I_0$], and the wavelength of (b) cDHIP-N-Br (d) cDHIP-N-Ph (f) cDHIP-N-DMA (h) cDHIP-N-

TPA (j) cDHIP-N-MTPA with different water fractions. [cDHIPs] = 10 μM, (cDHIP-N-Br, cDHIP-N-Ph: λ_{ex} = 420 nm, cDHIP-N-DMA: λ_{ex} = 470 nm, cDHIP-N-TPA, cDHIP-N-MTPA: λ_{ex} = 450 nm)

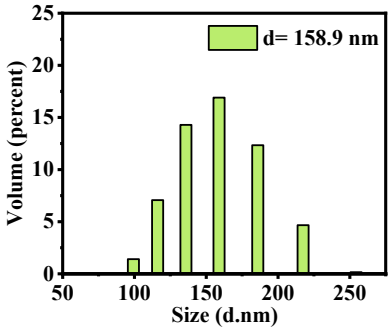


Fig. S32 The particle size distribution diagram of cDHIP-N-TPA. (f_w = 60%)

14.Cartesian coordinates

Table S2. Geometry Data for cDHIP-N-Br.

	X	Y	Z
C	1.251165	-1.16095	-0.31198
C	-0.02819	-0.79517	-0.04126
N	-0.31946	0.490077	0.322205
C	0.59414	1.51585	0.467618
C	1.952321	1.09373	0.170011
C	2.273497	-0.17811	-0.1927
N	-1.17056	-1.57946	-0.07597
C	-2.17342	-0.84427	0.254677
C	-1.77939	0.618774	0.5589
C	-3.54094	-1.34779	0.321828
C	-2.40781	1.611344	-0.41278
C	3.687552	-0.52828	-0.60563
O	3.965031	-0.40998	-1.79752
N	4.529058	-0.95046	0.340314
Br	1.650206	-2.93686	-0.82196
Br	3.269832	2.43867	0.339337
C	-4.57103	-0.59092	0.888708
C	-5.858	-1.1025	0.948092
C	-6.1317	-2.3654	0.440797
C	-5.11234	-3.12463	-0.12517
C	-3.82555	-2.62274	-0.18255
C	-3.06634	2.74288	0.052609
C	-3.63001	3.637995	-0.84725
C	-3.53819	3.410355	-2.21305

C	-2.87763	2.280868	-2.67896
C	-2.31486	1.384006	-1.78314
O	-2.06386	1.014147	1.859491
C	-1.54548	0.196025	2.909775
C	5.906063	-1.27288	-0.00126
O	0.252353	2.637687	0.813744
C	4.202195	-1.04281	1.754596
H	-4.37001	0.388989	1.298471
H	-6.64954	-0.51125	1.392853
H	-7.14022	-2.76014	0.485196
H	-5.32451	-4.1098	-0.52337
H	-3.03116	-3.20981	-0.62451
H	-3.13601	2.928717	1.115197
H	-4.1404	4.518741	-0.47486
H	-3.979	4.110578	-2.91331
H	-2.79987	2.094	-3.74368
H	-1.80267	0.508229	-2.16621
H	-1.8797	0.659867	3.833911
H	-1.93717	-0.82159	2.854091
H	-0.45437	0.175673	2.891381
H	6.034213	-1.24663	-1.07819
H	6.584827	-0.55265	0.460577
H	6.150062	-2.26987	0.368168
H	3.152367	-0.83155	1.934805
H	4.418461	-2.04999	2.113697
H	4.80541	-0.33332	2.324559

Table S3. Geometry Data for cDHIP-N-Ph.

	X	Y	Z
C	0.892104	1.296948	-0.18811
C	-0.33903	0.73593	-0.3011
N	-0.506	-0.61251	-0.47793
C	0.51769	-1.53106	-0.5729
C	1.846644	-0.95266	-0.45419
C	2.000308	0.392821	-0.27113
N	-1.57158	1.384012	-0.26786
C	-2.49629	0.504593	-0.41148
C	-1.94797	-0.93219	-0.55842
C	-3.92005	0.837437	-0.42329
C	-2.37995	-1.84159	0.58793
C	3.388872	0.984244	-0.20935
O	3.897729	1.378853	-1.26297
N	3.987752	1.061672	0.983804
C	1.065464	2.753164	0.065906

C	2.99351	-1.8981	-0.50756
C	1.559006	3.599758	-0.92593
C	1.718597	4.956276	-0.67674
C	1.39007	5.48162	0.566285
C	0.900061	4.644622	1.560555
C	0.739546	3.288198	1.311965
C	3.909284	-1.86299	-1.55751
C	4.977387	-2.75116	-1.59001
C	5.141229	-3.68344	-0.57517
C	4.229604	-3.72807	0.473411
C	3.160634	-2.84511	0.504368
C	-4.8872	-0.09975	-0.798
C	-6.229	0.250137	-0.81012
C	-6.62058	1.530902	-0.44546
C	-5.66438	2.469255	-0.07035
C	-4.32438	2.127707	-0.06106
C	-2.9064	-3.10332	0.339738
C	-3.29161	-3.91732	1.397143
C	-3.15201	-3.47895	2.706376
C	-2.62321	-2.2191	2.956281
C	-2.23954	-1.40317	1.902197
O	-2.28775	-1.53775	-1.76576
C	-1.95655	-0.8241	-2.95674
C	5.323567	1.625057	1.099753
O	0.281911	-2.7275	-0.74588
C	3.39405	0.621257	2.236308
H	1.81638	3.193905	-1.89682
H	2.098808	5.604465	-1.45818
H	1.515638	6.540964	0.759759
H	0.642491	5.047383	2.533614
H	0.360026	2.635574	2.090085
H	3.785168	-1.1378	-2.3523
H	5.681117	-2.71349	-2.4139
H	5.975702	-4.37516	-0.60045
H	4.351072	-4.45397	1.269531
H	2.449667	-2.88506	1.322017
H	-4.59612	-1.09774	-1.0948
H	-6.97063	-0.48221	-1.10639
H	-7.67062	1.799848	-0.45255
H	-5.96689	3.469443	0.216831
H	-3.57924	2.85545	0.232684
H	-3.01218	-3.45322	-0.67752
H	-3.70009	-4.90036	1.192632
H	-3.45375	-4.11588	3.529985

H	-2.51021	-1.8669	3.975044
H	-1.82968	-0.42198	2.116591
H	-2.28402	-1.45562	-3.77852
H	-2.47896	0.133569	-3.00759
H	-0.87997	-0.66223	-3.03456
H	5.690953	1.905597	0.118616
H	5.301234	2.506962	1.742959
H	5.998076	0.889083	1.541303
H	2.388188	0.243174	2.086192
H	4.003066	-0.16958	2.678647
H	3.35156	1.457765	2.936372

Table S4. Geometry Data for cDHIP-N-DMA.

	X	Y	Z
C	-0.2837	1.065484	-0.16798
C	-1.0513	-0.05126	-0.27368
N	-0.50024	-1.30451	-0.35495
C	0.850227	-1.57766	-0.36854
C	1.695883	-0.39953	-0.25656
C	1.134468	0.843468	-0.15779
N	-2.44132	-0.12532	-0.33573
C	-2.77992	-1.35909	-0.44389
C	-1.56931	-2.31815	-0.4655
C	-4.17145	-1.80012	-0.53666
C	-1.55208	-3.27397	0.72288
C	2.04577	2.050119	-0.16608
O	2.524526	2.397692	-1.24995
N	2.271876	2.691361	0.986164
C	-0.88296	2.420829	-0.07655
C	3.163226	-0.62574	-0.24534
C	-0.68056	3.371795	-1.0755
C	-1.24262	4.634981	-1.00031
C	-2.03438	5.016675	0.097489
C	-2.24852	4.048421	1.095125
C	-1.67897	2.789756	1.006146
C	3.937528	-0.35772	0.879817
C	5.308942	-0.5586	0.884178
C	5.974886	-1.05547	-0.24898
C	5.188632	-1.31499	-1.38747
C	3.820525	-1.11345	-1.37402
C	-5.19933	-0.87949	-0.30128
C	-6.52294	-1.26965	-0.39229
C	-6.84193	-2.58276	-0.72333
C	-5.82982	-3.50194	-0.96227

C	-4.50065	-3.11727	-0.8687
C	-1.40007	-4.64295	0.540086
C	-1.38557	-5.4946	1.637289
C	-1.52092	-4.9862	2.921334
C	-1.6695	-3.61747	3.10589
C	-1.68541	-2.7648	2.01201
O	-1.47313	-3.06071	-1.64123
C	-1.47012	-2.3267	-2.86506
C	3.116637	3.874488	1.011826
N	-2.56367	6.296502	0.201967
C	-3.67944	6.488864	1.116085
C	-2.6348	7.094911	-1.01232
N	7.341975	-1.30157	-0.23958
C	8.010421	-1.43113	-1.52551
C	8.133914	-0.64674	0.790572
O	1.259535	-2.73639	-0.4647
C	1.753374	2.274447	2.277918
H	-0.07759	3.121052	-1.94082
H	-1.05902	5.32441	-1.81216
H	-2.85898	4.273805	1.958156
H	-1.86092	2.076744	1.802703
H	3.463616	0.008508	1.783863
H	5.855732	-0.33155	1.788539
H	5.64305	-1.68121	-2.29726
H	3.252209	-1.32751	-2.27274
H	-4.94968	0.141187	-0.04257
H	-7.31055	-0.54952	-0.20404
H	-7.87979	-2.88734	-0.79454
H	-6.0739	-4.52478	-1.22399
H	-3.72386	-3.84156	-1.0697
H	-1.28868	-5.04522	-0.45702
H	-1.26466	-6.56082	1.483563
H	-1.50979	-5.65289	3.776025
H	-1.77454	-3.2099	4.104693
H	-1.79962	-1.69871	2.175614
H	-1.37893	-3.06978	-3.65313
H	-2.39979	-1.7699	-3.00084
H	-0.61986	-1.64402	-2.91554
H	3.372406	4.16517	-0.00166
H	2.5859	4.693555	1.500253
H	4.033214	3.671327	1.57027
H	-4.54559	5.863471	0.863399
H	-3.39158	6.273021	2.144508
H	-3.98809	7.531211	1.081032

H	-1.64265	7.283679	-1.4213
H	-3.24431	6.623105	-1.79404
H	-3.07296	8.061272	-0.77326
H	7.627858	-2.28295	-2.08711
H	7.90683	-0.53371	-2.14925
H	9.069868	-1.6092	-1.35566
H	8.055611	0.447623	0.752581
H	7.838627	-0.97501	1.786794
H	9.178547	-0.91985	0.659465
H	1.190857	1.3495	2.198909
H	2.581711	2.117226	2.971862
H	1.102545	3.049101	2.688038

Table S5. Geometry Data for cDHIP-N-TPA.

	X	Y	Z
C	1.035117	0.379133	-0.31378
C	1.097732	1.733986	-0.37629
N	-0.03159	2.508007	-0.42729
C	-1.32339	2.027271	-0.42876
C	-1.41832	0.57584	-0.36697
C	-0.28273	-0.18455	-0.31168
N	2.240111	2.530204	-0.41059
C	1.876334	3.759521	-0.48513
C	0.341529	3.936329	-0.50037
C	2.826017	4.870291	-0.53821
C	-0.17097	4.708158	0.711168
C	-0.38886	-1.6913	-0.30832
O	-0.33961	-2.2778	-1.3942
N	-0.51615	-2.31253	0.869088
C	2.263079	-0.45144	-0.19708
C	-2.78422	-0.00589	-0.34271
C	2.712974	-1.23558	-1.25818
C	3.858056	-2.00578	-1.14122
C	4.597109	-2.0057	0.043296
C	4.151473	-1.22026	1.107727
C	2.998145	-0.46264	0.987354
C	-3.23442	-0.85481	-1.35214
C	-4.51276	-1.38968	-1.32084
C	-5.37818	-1.10062	-0.26605
C	-4.93122	-0.25095	0.74932
C	-3.66091	0.294362	0.701603
C	4.177146	4.628713	-0.26359
C	5.096599	5.660453	-0.31433
C	4.683269	6.947195	-0.64431

C	3.346336	7.195537	-0.92279
C	2.41885	6.166	-0.86863
C	-1.03222	5.78792	0.559596
C	-1.48759	6.477436	1.676001
C	-1.08855	6.093157	2.948306
C	-0.23016	5.011965	3.101576
C	0.227361	4.322335	1.988416
O	-0.137	4.546307	-1.65823
C	0.257202	3.961442	-2.89934
C	-0.62721	-3.76153	0.925776
N	5.771148	-2.78247	0.159968
C	6.078468	-3.43439	1.381698
C	6.664862	-2.89203	-0.93664
N	-6.67802	-1.65197	-0.22447
C	-7.76934	-0.87156	0.23613
C	-6.90196	-2.98539	-0.6541
C	7.380337	-3.4187	1.882913
C	7.681345	-4.06844	3.071058
C	6.689422	-4.7285	3.785353
C	5.39056	-4.73901	3.29205
C	5.085641	-4.10568	2.096344
C	6.990719	-1.77146	-1.70124
C	7.862996	-1.88536	-2.77376
C	8.436294	-3.11072	-3.08998
C	8.11954	-4.22631	-2.32493
C	7.235128	-4.12316	-1.2613
C	-8.7288	-1.42944	1.081564
C	-9.80185	-0.66844	1.521539
C	-9.92709	0.661641	1.140353
C	-8.96881	1.221451	0.30456
C	-7.90214	0.461804	-0.15279
C	-8.00819	-3.29638	-1.4452
C	-8.23272	-4.6034	-1.85226
C	-7.3524	-5.61581	-1.49178
C	-6.24548	-5.30702	-0.71083
C	-6.02355	-4.00528	-0.28654
O	-2.2826	2.797859	-0.48274
C	-0.54446	-1.64103	2.158736
H	2.155718	-1.25271	-2.18688
H	4.18196	-2.6125	-1.97797
H	4.712097	-1.19881	2.034148
H	2.67051	0.140799	1.826405
H	-2.58343	-1.09163	-2.18434
H	-4.84162	-2.03331	-2.12748

H	-5.58242	-0.01868	1.583086
H	-3.33771	0.951209	1.500969
H	4.495906	3.627439	-0.00455
H	6.139348	5.463669	-0.09454
H	5.404823	7.755217	-0.68386
H	3.021573	8.195693	-1.18444
H	1.383207	6.371587	-1.10094
H	-1.35195	6.0887	-0.4282
H	-2.16063	7.317285	1.546847
H	-1.4449	6.633077	3.818117
H	0.087166	4.703157	4.090876
H	0.897162	3.480811	2.128386
H	-0.22912	4.552843	-3.67077
H	1.339548	4.009014	-3.03719
H	-0.08039	2.926208	-2.97384
H	-0.65513	-4.16791	-0.07944
H	0.226142	-4.1822	1.461609
H	-1.54117	-4.03993	1.453634
H	8.15808	-2.89568	1.339372
H	8.698664	-4.04664	3.445616
H	6.926119	-5.2305	4.716322
H	4.606773	-5.25611	3.834289
H	4.072908	-4.1325	1.712224
H	6.55973	-0.80879	-1.45321
H	8.105547	-1.00433	-3.35746
H	9.123003	-3.19533	-3.92424
H	8.554429	-5.19061	-2.56318
H	6.983794	-5.00115	-0.67817
H	-8.63235	-2.46227	1.39449
H	-10.5386	-1.11795	2.178014
H	-10.7632	1.255757	1.490577
H	-9.05657	2.256237	-0.0073
H	-7.16755	0.902944	-0.81586
H	-8.69311	-2.51092	-1.74166
H	-9.09781	-4.82788	-2.46626
H	-7.52692	-6.63518	-1.81599
H	-5.55311	-6.08763	-0.41591
H	-5.16564	-3.77636	0.334435
H	-0.39982	-0.57111	2.050626
H	-1.50273	-1.81806	2.651176
H	0.249724	-2.03683	2.794548

Table S6. Geometry Data for cDHIP-N-MTPA.

	X	Y	Z

C	1.082699	0.898124	-0.35246
C	1.036259	2.241162	-0.54537
N	-0.15214	2.918724	-0.63697
C	-1.40112	2.340533	-0.56415
C	-1.37993	0.897639	-0.37121
C	-0.18664	0.237498	-0.26717
N	2.111359	3.11552	-0.68779
C	1.650452	4.300661	-0.86663
C	0.10664	4.358256	-0.85098
C	2.507456	5.470569	-1.05617
C	-0.43427	5.198779	0.301427
C	-0.17342	-1.26464	-0.11354
O	-0.09687	-1.95422	-1.13531
N	-0.2315	-1.7719	1.122999
C	2.373227	0.178331	-0.18727
C	-2.69478	0.214444	-0.28536
C	2.871741	-0.66104	-1.18178
C	4.073281	-1.33059	-1.02129
C	4.828181	-1.17689	0.14665
C	4.329949	-0.33393	1.146439
C	3.12328	0.323739	0.979237
C	-3.08633	-0.73206	-1.22975
C	-4.32051	-1.35773	-1.1553
C	-5.21024	-1.06498	-0.11724
C	-4.81759	-0.11576	0.836293
C	-3.59099	0.515271	0.742428
C	3.883273	5.3559	-0.82533
C	4.715906	6.445501	-1.00392
C	4.189897	7.664411	-1.41998
C	2.827512	7.786729	-1.65558
C	1.986884	6.698856	-1.47351
C	-1.40427	6.170042	0.086074
C	-1.88263	6.924257	1.149804
C	-1.39868	6.712711	2.433056
C	-0.43154	5.739747	2.650728
C	0.049273	4.986334	1.590004
O	-0.44517	4.821676	-2.04386
C	-0.0525	4.145102	-3.23774
C	-0.21844	-3.21183	1.326033
N	6.051361	-1.8446	0.311112
C	6.500766	-2.23461	1.604091
C	6.848302	-2.19321	-0.81505
N	-6.45535	-1.70279	-0.02856
C	-7.5741	-1.05277	0.565215

C	-6.66367	-2.97587	-0.63298
C	7.806992	-1.95473	2.009381
C	8.259382	-2.35204	3.252723
C	7.409725	-3.0241	4.13062
C	6.103881	-3.30111	3.741458
C	5.664717	-2.91593	2.479755
C	7.163345	-1.24241	-1.78875
C	7.943007	-1.58084	-2.87704
C	8.448018	-2.87446	-3.00881
C	8.15446	-3.82505	-2.03848
C	7.350456	-3.48024	-0.95704
C	-8.36696	-1.73184	1.492122
C	-9.47159	-1.12276	2.055231
C	-9.80096	0.189672	1.71858
C	-9.01502	0.878599	0.801476
C	-7.91774	0.249341	0.224225
C	-5.83058	-4.05383	-0.32644
C	-6.03541	-5.28882	-0.90907
C	-7.09314	-5.48292	-1.79805
C	-7.93805	-4.42118	-2.09908
C	-7.71103	-3.17603	-1.52192
O	-2.42062	3.025077	-0.6646
C	-0.27611	-0.97858	2.340948
O	7.944625	-3.36827	5.339119
C	7.11744	-4.06783	6.260051
O	-10.9037	0.709091	2.334295
C	-11.2799	2.042629	2.01494
O	9.216583	-3.10954	-4.11295
C	9.750039	-4.41589	-4.28795
O	-7.21869	-6.74024	-2.31479
C	-8.2738	-6.97995	-3.23751
H	2.308343	-0.80272	-2.09636
H	4.426758	-1.98147	-1.81084
H	4.893444	-0.18845	2.059435
H	2.761825	0.972236	1.769664
H	-2.42289	-0.97685	-2.05006
H	-4.59667	-2.07364	-1.91868
H	-5.478	0.126995	1.659118
H	-3.31778	1.246985	1.494373
H	4.290193	4.407462	-0.49966
H	5.778798	6.347055	-0.81688
H	4.843677	8.517679	-1.55955
H	2.414657	8.733442	-1.98345
H	0.929664	6.805915	-1.67239

H	-1.78987	6.336244	-0.90993
H	-2.64018	7.678731	0.971281
H	-1.77317	7.303186	3.261412
H	-0.04679	5.566549	3.649078
H	0.805437	4.231897	1.77788
H	-0.58331	4.642132	-4.04553
H	1.022986	4.227444	-3.40881
H	-0.3428	3.093301	-3.21014
H	-0.25289	-3.71878	0.367762
H	0.687796	-3.50794	1.858664
H	-1.08406	-3.50637	1.921956
H	8.47428	-1.42427	1.340093
H	9.274122	-2.13839	3.568012
H	5.423193	-3.82671	4.397362
H	4.649973	-3.14983	2.179528
H	6.790345	-0.22959	-1.69164
H	8.186356	-0.84509	-3.63478
H	8.530698	-4.83626	-2.11316
H	7.118378	-4.23127	-0.21098
H	-8.11516	-2.74889	1.769398
H	-10.0896	-1.64912	2.773408
H	-9.24944	1.894747	0.514662
H	-7.32059	0.789937	-0.50069
H	-5.01321	-3.91857	0.372298
H	-5.38945	-6.12705	-0.67491
H	-8.76629	-4.53995	-2.78435
H	-8.36795	-2.35037	-1.76999
H	-0.24144	0.083636	2.122628
H	-1.19425	-1.1933	2.891362
H	0.575213	-1.23217	2.975705
H	7.73286	-4.24472	7.138886
H	6.246269	-3.47179	6.541811
H	6.789176	-5.02523	5.848807
H	-12.1693	2.251011	2.60479
H	-10.4927	2.750875	2.283724
H	-11.5171	2.1435	0.953373
H	10.32269	-4.3829	-5.21172
H	10.4108	-4.68767	-3.46147
H	8.954565	-5.15906	-4.38099
H	-8.18621	-8.02478	-3.52562
H	-9.24934	-6.81206	-2.77511
H	-8.17464	-6.34949	-4.1241

15. Biological experiment results

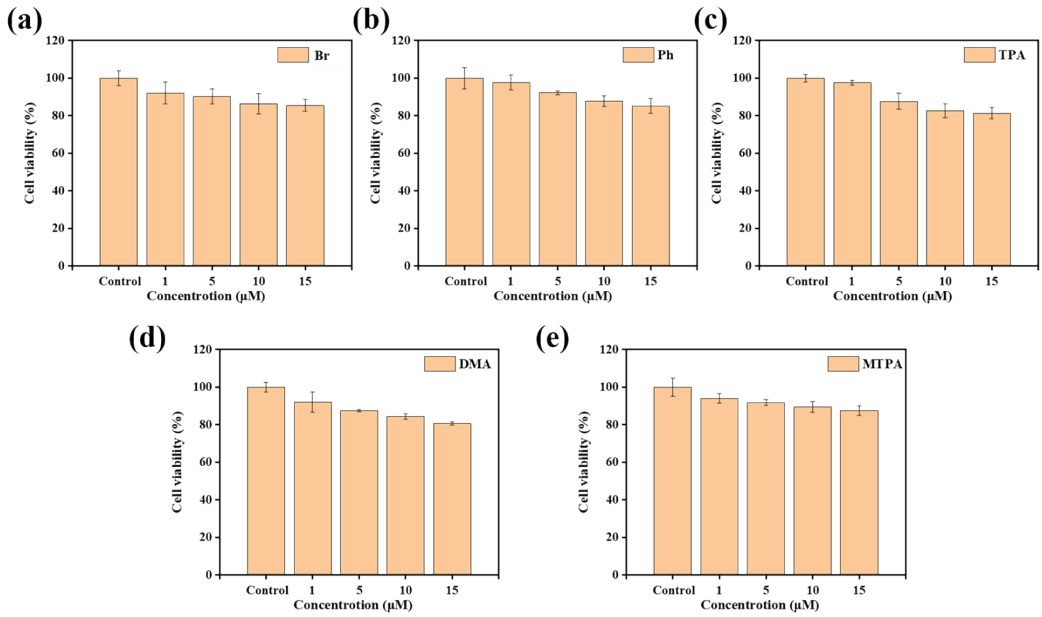


Fig. S33. Cell viabilities of 4T1 cells after incubation with different concentrations of cDHIPs determined by MTT assay.

Table S7. Cell imaging SBR of different compounds of cDHIPs.

Compounds	Cell		$SBR_{R/G}$
	SBR_R	SBR_G	
cDHIP-N-Br	508.13	450	1.13
cDHIP-N-Ph	211.03	114.5	1.84
cDHIP-N-DMA	188.64	95.35	1.98
cDHIP-N-TPA	180.59	73.57	2.45
cDHIP-N-MTPA	528.26	159.39	3.31

SBR_R: The SBR of the red channel (cDHIPs), SBR_G: the SBR of the green channel, $SBR_{R/G}$ = SBR_R/ SBR_G

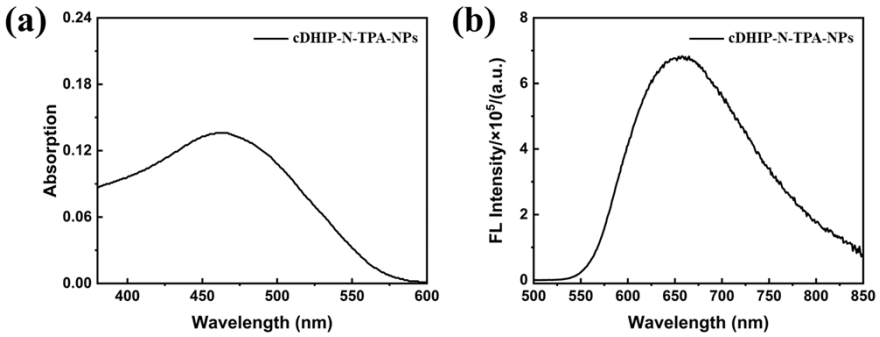


Fig. S34. (a) UV absorption spectra and (b) FL spectra of cDHIP-N-TPA-NPs. [cDHIP-N-TPA-NPs] = 10 μM. (λ_{ex} = 450 nm)

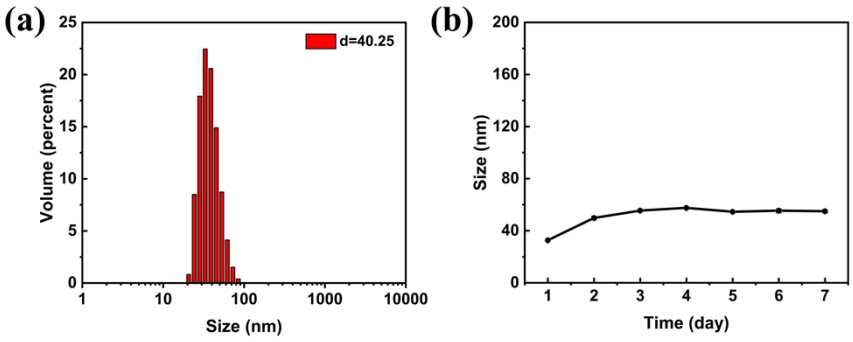


Fig. S35. (a) Dynamic laser scattering size of cDHIP-N-TPA-NPs. (b) Stability of cDHIP-N-TPA-NPs. [cDHIP-N-TPA-NPs] = 10 μM

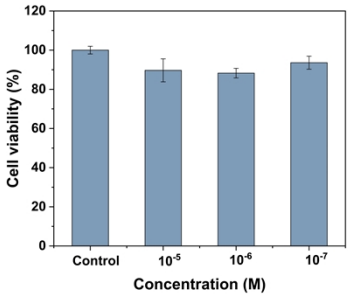


Fig. S36. Cell viabilities of 4T1 cells after incubation with different concentrations of cDHIP-N-TPA-NPs determined by MTT assay. [cDHIP-N-TPA-NPs] = 10 μM

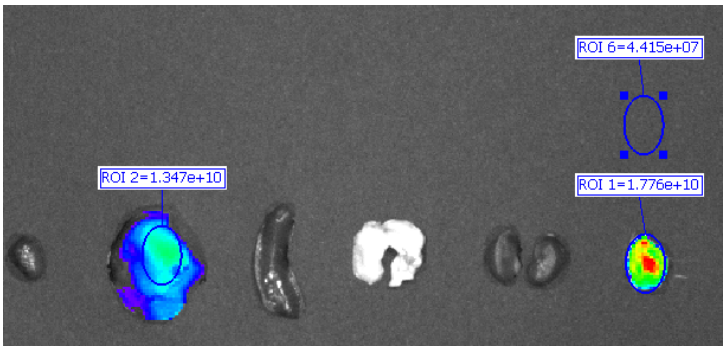


Fig. S37. *Ex vivo* fluorescence images of major organs and tumors after intravenous injection of cDHIP-N-TPA-NPs.