

Supporting Information

BSA-Coated Fluorescent Organic-Inorganic Hybrid Silica Nanoparticles: Preparation, and Drug Delivery

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General information

Triphenylamine (TPA, 99%), phosphorus oxychloride (POCl_3), SiO_2 , surface area $300 \text{ m}^2/\text{g}$, particle sizes 50-60 nm, density 1.9 g/cm^3 , potassiumiodide (KI, 99%), Potassium Iodate(KIO_3 , 99%), Bovine Serum Albumin (BSA, 98%), Methylacrylate (MA, 98%), and Palladium acetate ($\text{Pd}(\text{OAc})_2$, 99%), 1,3-bis(diphenylphosphino)propane (DPPP, 98%), Triethylamine(Et_3N , 99%) purchased from Aladdin Co. Other commercial reagents were purchased from Aladdin Co. and Energy Chemical Co. and used without further purification unless otherwise stated. $\text{SiO}_2\text{-NH}_2$ nanoparticles were obtained by the documented method. (*J. Mater. Chem.*, **2012**, 22, 18961-18967)

Room temperature ^1H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra were recorded on a MERCURY spectrometer with CDCl_3 as the solvent and tetramethylsilane (TMS) as the internal reference.

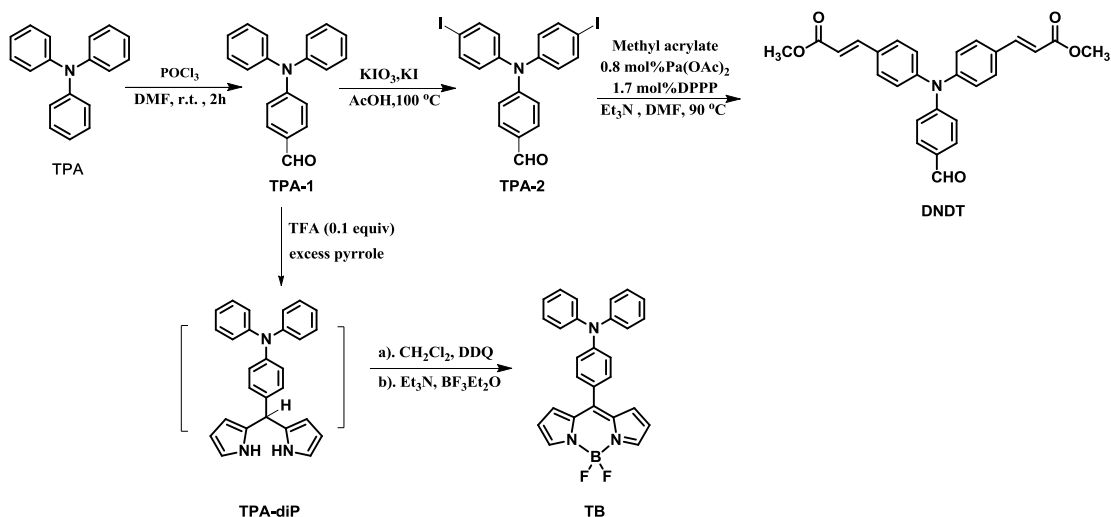
Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet AVATAR 360 TF-IR spectrophotometer using KBr tablets. UV-visible absorption spectra (UV) were recorded on a TU-1901 spectrometer from 190 to 1100 nm.

Fluorescence spectra were measured using a PE LS-55 Luminescence/Fluorescence Spectrophotometer.

Circular dichroism were measured using a JASCO J805 Spectrometer.

Particle size measurements process were performed on a Zetasizer Nano ZS dynamic light scattering (DLS) system.

The morphology of $\text{DNDT}\&\text{SiO}_2\text{-NH}_2$ and $\text{BSA}\&\text{DNDT}\&\text{SiO}_2\text{-NH}_2$ was observed by scanning electron microscopy (SEM, ZEISS ULTRA PLUS). All the samples were prepared according to the standard methods.



Scheme S1 The synthetic route of **TPA-1**, **TPA-2** and **DNDT**.

Synthesis of TPA-1

Triphenylamine (0.49 g, 2 mmol) was dissolved in DMF (8 mL) and placed in a 100 mL flask. phosphorousoxychloride (0.78 g, 5mmol) was added dropwise in ice bath, and the reaction mixture is stirred for 10 minutes at 0 °C. And then the mixture was refluxed at 45 °C for 8 h under N₂ atmosphere. The reaction solution was quenched with cold water (100 mL) and white solid was obtained. The residue was purified by column chromatography on silica gel (300-400 mesh) with a mixture of ethyl acetate and petroleum ether as eluent (1:100 by volume), leading to the purified TPA-1 0.44 g, yield: 75%. ¹H NMR (CDCl₃): δ 9.76 (s, 1H), 7.70 (d, J = 8.8 Hz, 2H), 7.18-7.24 (d, J = 8.4 Hz, 6H), 7.42 (d, J = 8.0 Hz, 4H), 7.71 (d, J = 8.4 Hz, 2H),.

Synthesis of TPA-2

In a 50 mL two necked round bottom flask, 1.6 g(6 mmol, 1.0 equiv) of 4-(diphenylamino)benzaldehyde and 2.241 g(13.5 mmol, 2.25equiv) of potassium iodide were dissolved in the mixture of acetic acid (24 mL) and H₂O (2.4 mL) under N₂. The mixture was warmed and stirred to yellow transparent solution, then potassium iodate 2.889 g (13.5 mmol, 2.25 equiv) was added within several times. The reaction mixture was warmed to reflux and stirred for 1 h. Then the mixture was cooled to room temperature and pour in distilled water, and dark yellow solid was obtained. The crude product was purified by column chromatography directly to afford 4-(bis(4-iodophenyl)amino)benzaldehyde (TPA-2) as an orange solid (2.6 g, 5.1 mmol, 84.8% yield). M.P.: 146-151 °C; ¹H NMR (600 MHz, CDCl₃) δ (TMS, ppm): 9.84 (s, 1H), 7.71 (d, J = 8.3 Hz, 2H), 7.63 (d, J = 8.5 Hz, 4H), 7.05 (d, J = 8.3 Hz, 2H), 6.89 (d, J = 8.4 Hz, 4H). ¹³C NMR (150 MHz, CDCl₃) δ(ppm) 190.35, 152.17, 145.69, 138.85, 131.34, 130.31, 127.60, 120.75, 88.75. MS (FAB): m/z = 524.91 [M+H]⁺

Synthesis of TB

Pyrrole (5 mL, 72 mmol) and TPA-1 (0.786 g, 2.88 mmol) are added to a dry 100 mL round-bottomed flask and degassed with a stream of N₂ for 5 min. TFA (22.2 μL, 0.5 mmol) was then added, and the solution is stirred under N₂ at room temperature. TLC analysis indicates that the disappearance of spots corresponds to TPA-1 and appearance of a new spot corresponds to compound TPA-diP. The solvent is removed on a rotary evaporator under vacuum, and the crude compound is passed through flash silica gel column chromatography with a mixture of ethyl acetate and petroleum ether as eluent (1:6 by volume). The resultant compound TPA-diP (0.389g, 1 mmol) is dissolved in freshly distilled dichloromethane and oxidized with DDQ (272.4 mg, 1.2 mmol) for 30 min at room temperature. The reaction mixture is then treated with a small amount of Et₃N (5.6 mL, 40 mmol) followed by BF₃•OEt₂ (6.3 mL, 50 mmol), and the mixture is stirred for an additional 30 min at room temperature. The solvent is removed in a rotary evaporator, and the resultant crude compound is purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1) and afforded pure TB (144.8mg, 26%) as a purple solid. Mp 212-214 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.90 (s, 2H), 7.40 (m, 6H), 7.23-7.06 (m, 10H), 6.55 (s, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 150.94, 147.52, 146.47, 142.77, 134.63, 132.25, 131.00, 129.67, 126.22, 125.94, 124.70, 120.02, 117.95 ppm. MS (FAB): m/z = 435.17 [M+H]⁺. IR (KBr) : 3105, 3059, 3036, 1587, 1558, 1533, 1488, 1412, 1388, 1332, 1294, 1261, 1224, 1192, 1118, 1076, 980, 911, 757, 742, 696 cm⁻¹.

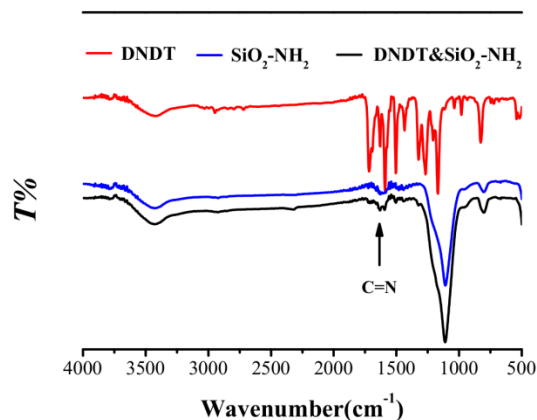


Fig. S1 FT-IR spectrum of DNDT, SiO₂-NH₂, and DNDT&SiO₂-NH₂.

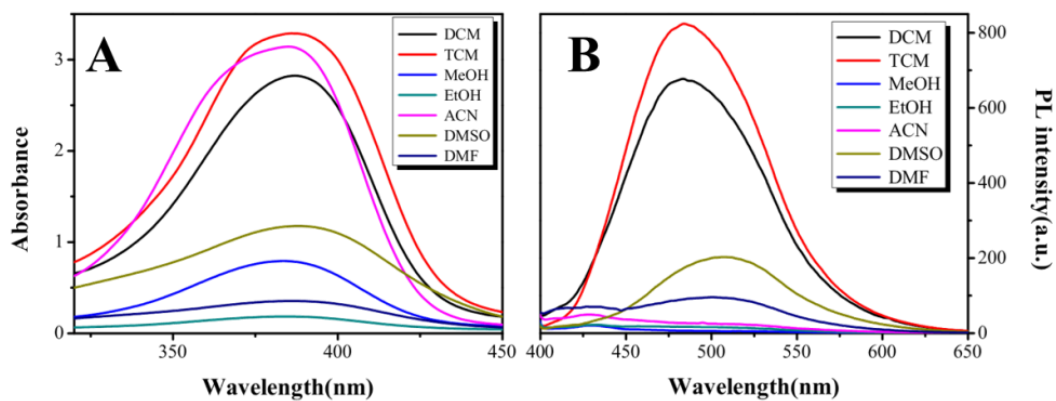


Fig. S2 (A) Absorbance spectra of DNDT&SiO₂-NH₂ in different solvents. (B) Emission spectra of DNDT&SiO₂-NH₂ in different solvents. (solution concentration: 5×10^{-3} g/L, $\lambda_{\text{ex}} = 370$ nm).

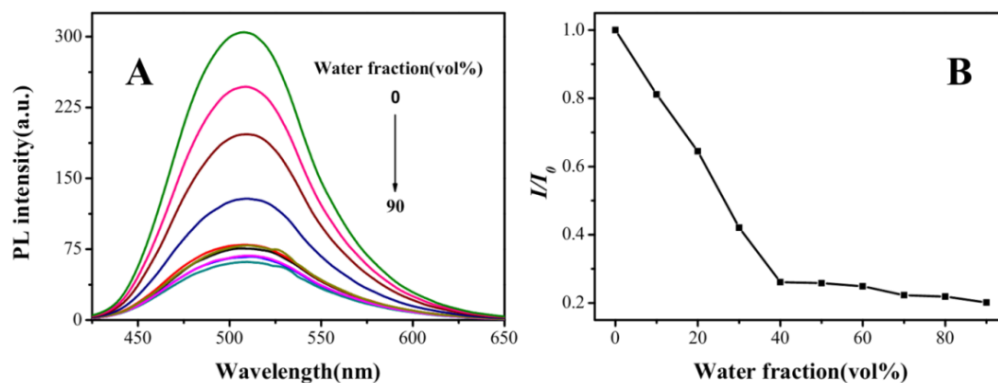


Fig. S3 (A) Emission spectra of DNDT&SiO₂-NH₂ in DMSO/water mixtures. (B) Plots of maximum emission intensity (I/I_0) of DNDT&SiO₂-NH₂ versus water fraction in the DMSO/H₂O mixture. (solution concentration: 5×10^{-3} g/L, $\lambda_{\text{ex}} = 370$ nm).

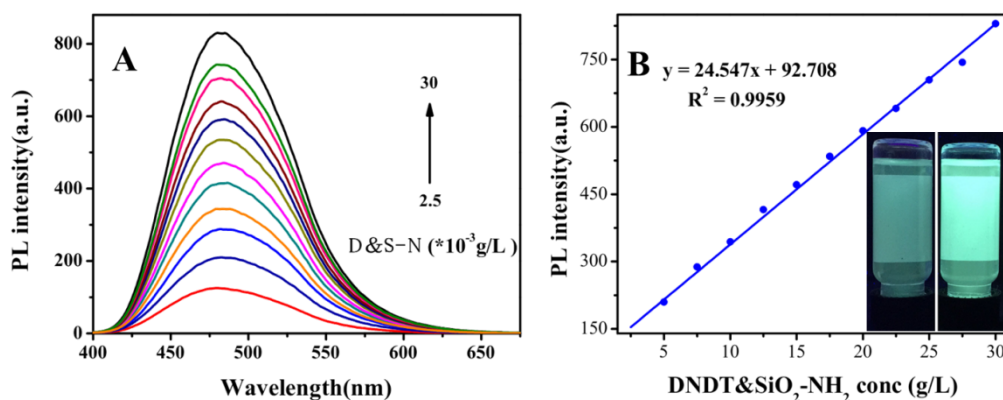


Fig. S4 (A) Emission spectra of different mass concentration DNDT&SiO₂-NH₂ in CHCl₃. (B) Plot of PL enhancement versus DNDT&SiO₂-NH₂ concentration. (I denotes the peak PL intensity and I_0 denotes the peak PL intensity of DNDT&SiO₂-NH₂ concentration = 2.5-30 × 10⁻³ g/L. solution concentration: 5 × 10⁻³ g/L, λ_{ex} = 370 nm)

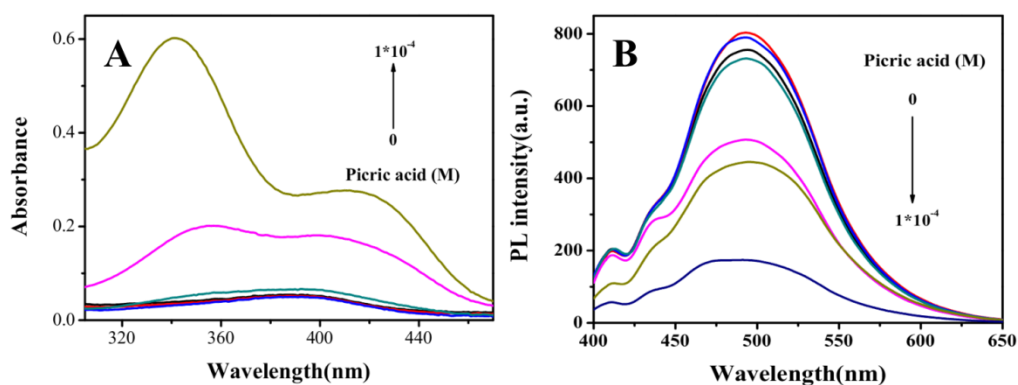


Fig. S5 (A) Normalized absorption spectra of DNDT&SiO₂-NH₂ at different PA concentrations. (B) Emission spectra of DNDT&SiO₂-NH₂ at different PA concentrations. (DNDT&SiO₂-NH₂ solution concentration: 5 × 10⁻³ g/L, λ_{em} = 370 nm)

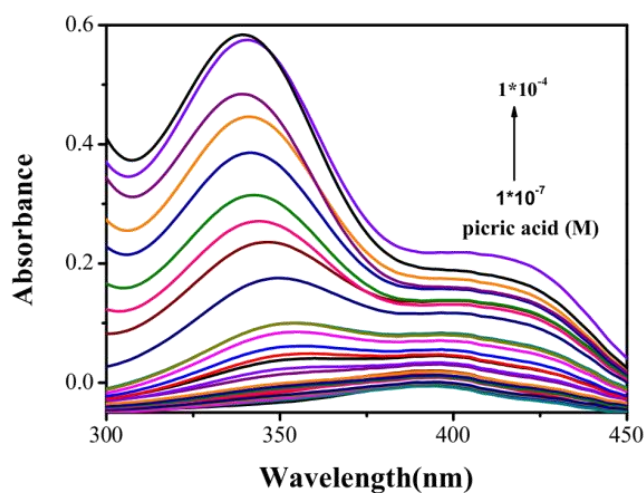


Fig. S6 Normalized absorption spectra of DNDT&SiO₂-NH₂ at different PA concentrations.

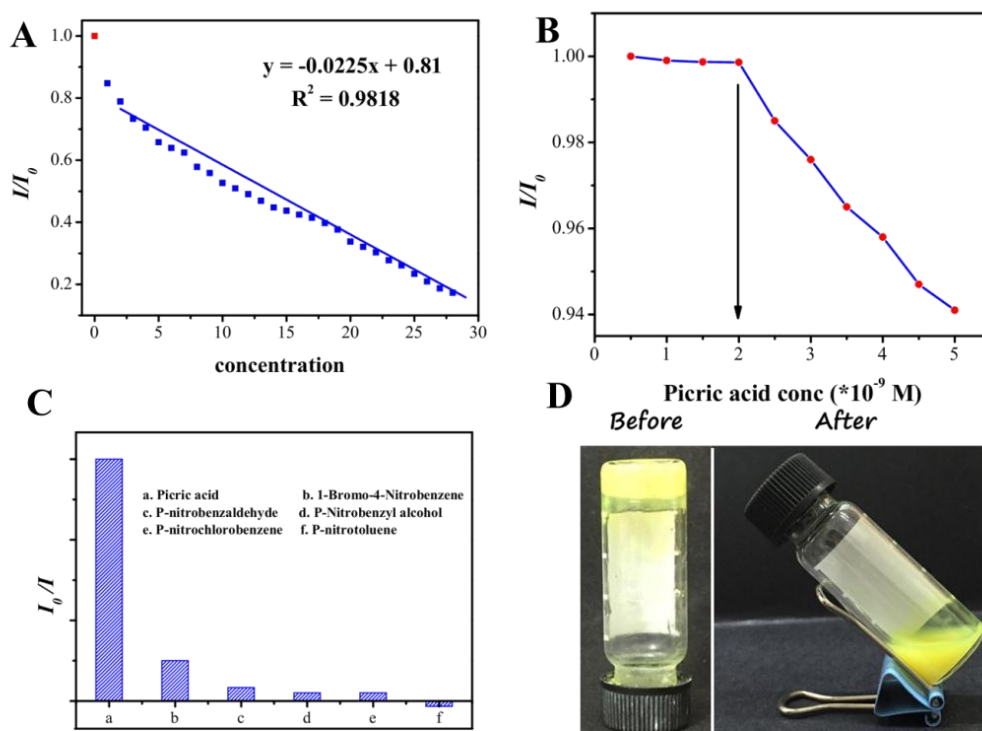


Fig. S7 (A) The relative PL intensity (I/I_0) of DNDT&SiO₂-NH₂ at different PA concentrations. (B) The plot of detection limit analysis of DNDT&SiO₂-NH₂ toward PA. ($D_L = 2 \times 10^{-9}$ M = 2 PPb) (C) Selectivity graph of DNDT&SiO₂-NH₂ toward various nitro derivatives. (D) Photograph of gel of DNDT&SiO₂-NH₂ (on the left) and DNDT&SiO₂-NH₂ within PA (on the right).

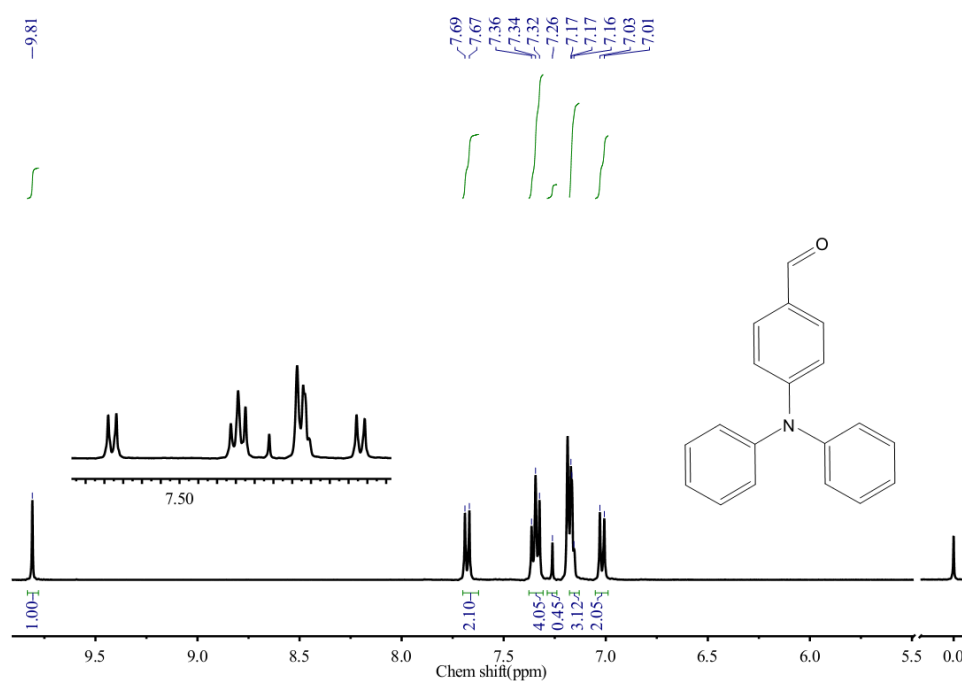


Fig. 8 ¹H NMR spectra of TPA-1 in CDCl₃.

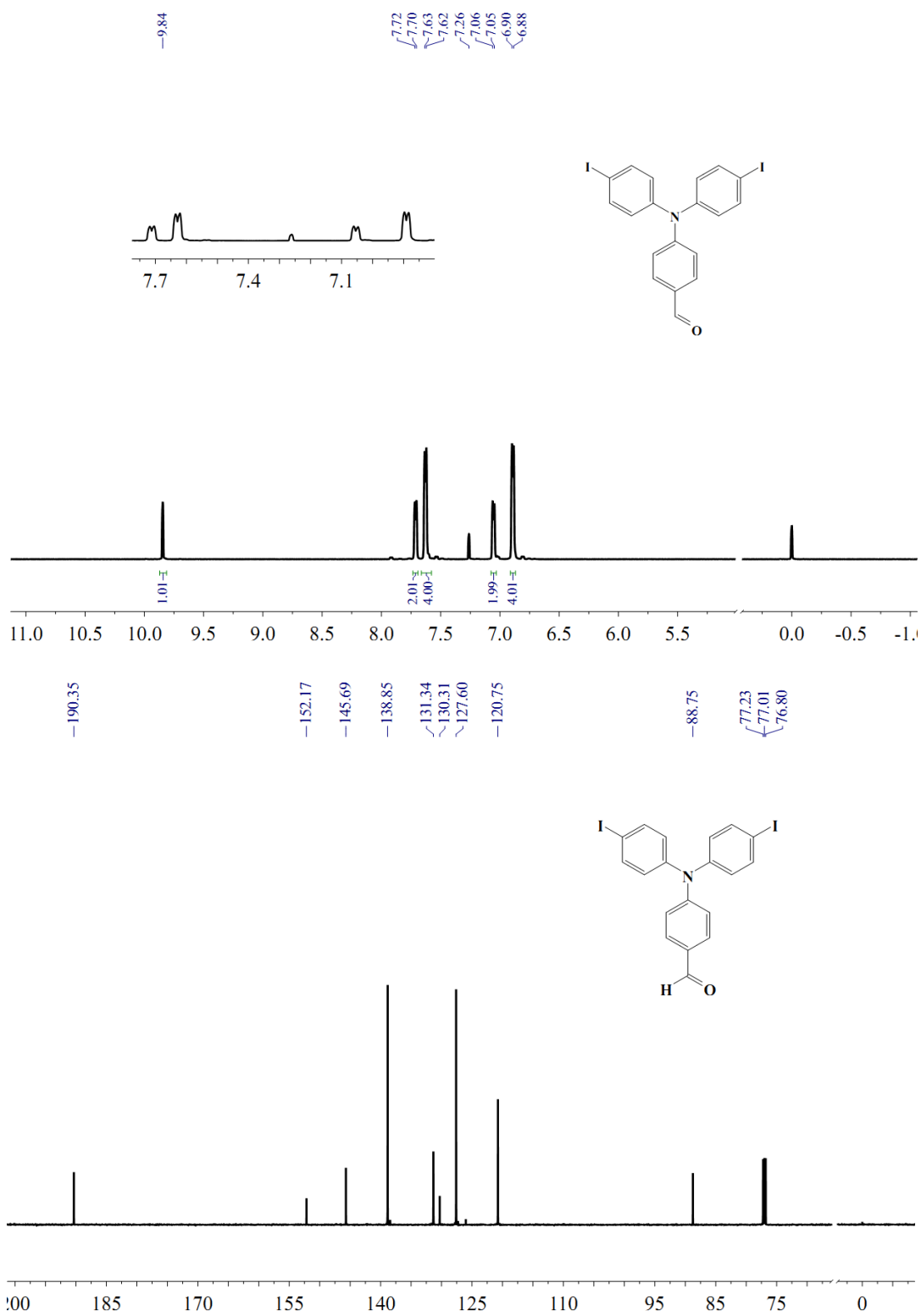


Fig. 9 ¹H and ¹³C NMR spectra of TPA-2 in CDCl₃.

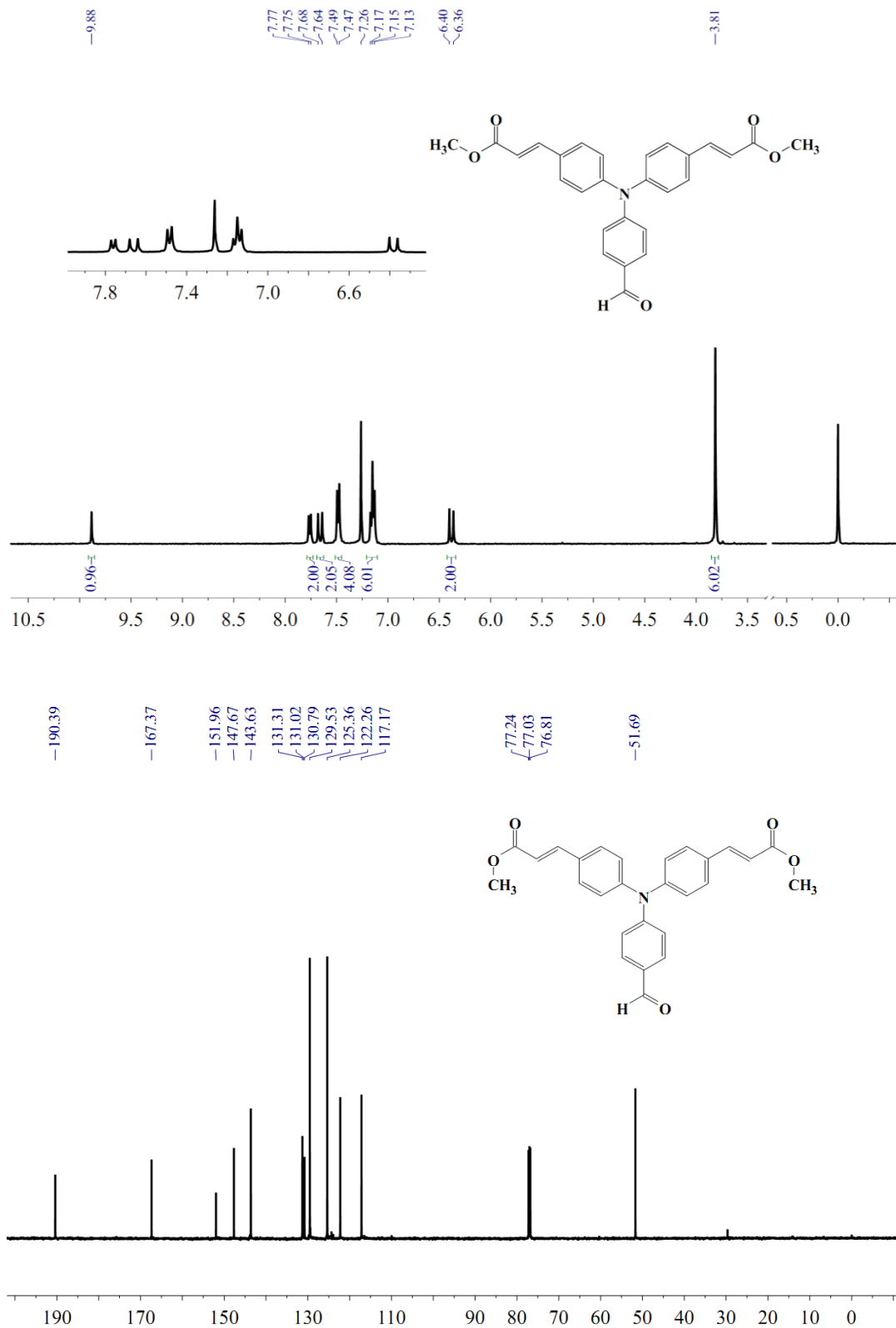


Fig. 10 ^1H and ^{13}C NMR spectra of DNNDT in CDCl_3 .

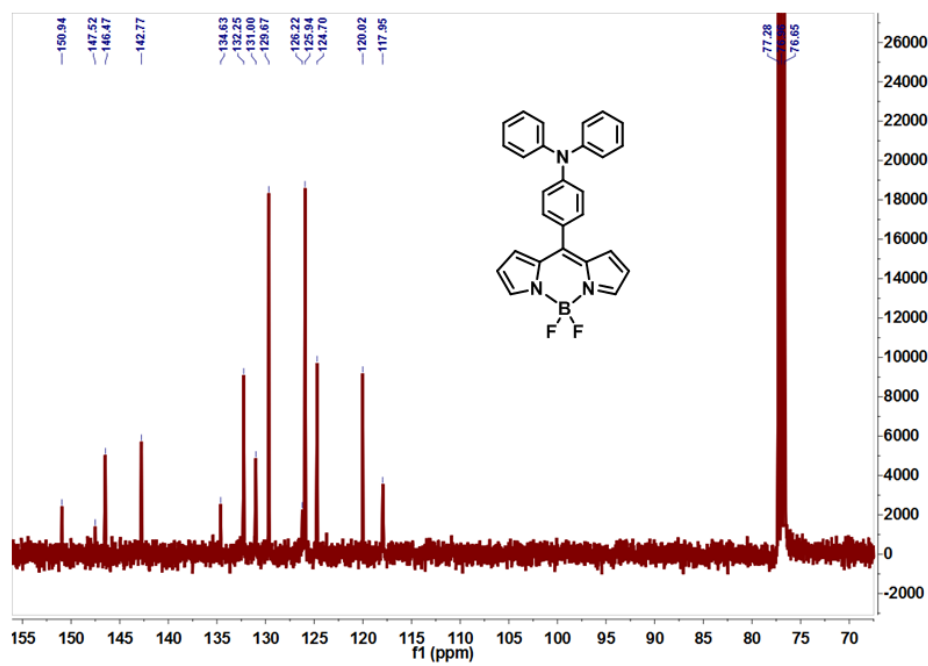
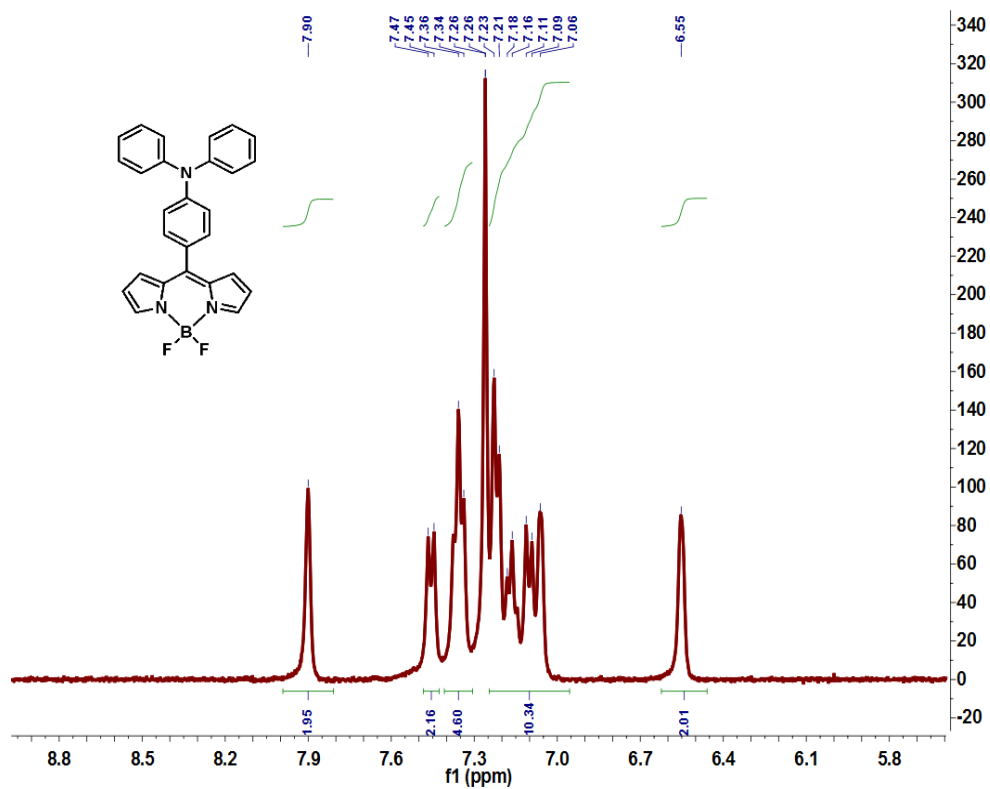


Fig. 11 ^1H and ^{13}C NMR spectra of TB in CDCl_3 .