Supplementary Information (SI) for Journal of Materials Chemistry B.

Supporting Information for

Uncovering Light-Induced Emission Enhancement in a Dual-Emissive Photosensitizer for Real-Time Photodynamic Theranostics

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Supplementary Figures

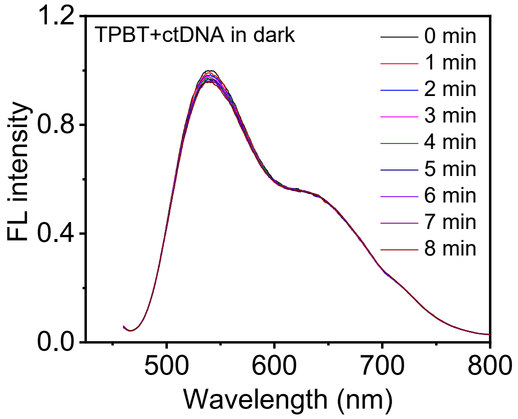

Figure S1 Fluorescence change of TPBT and ctDNA mixture solution in state II (ctDNA = 20 μg mL^{-1}) in dark (460 nm, 25 mW cm^{-2})

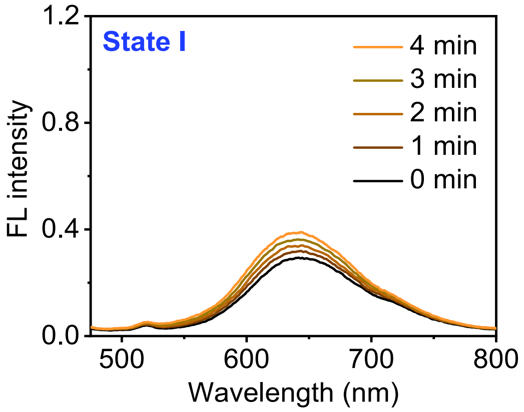

Figure S2 Fluorescence change of TPBT and ctDNA mixture solution in state I (ctDNA = 20 μg mL^{-1}) upon blue light illumination (460 nm, 25 mW cm^{-2})

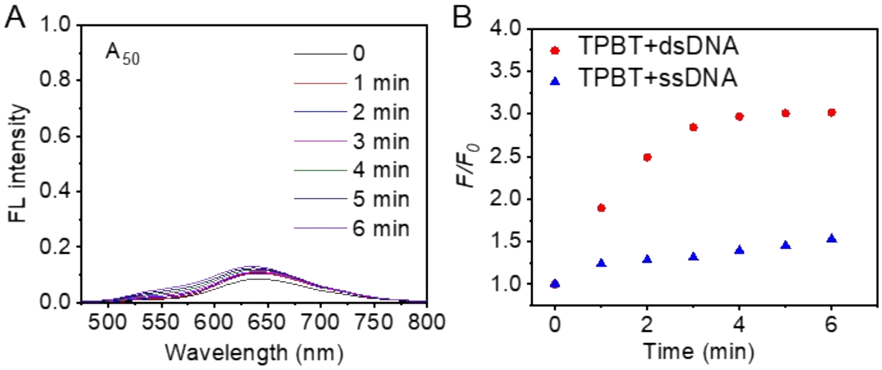

Figure S3. (A) Fluorescence change of TPBT (10 μM) and ssDNA (20 μM) mixture solution upon blue light illumination. (B) Plots of relative fluorescence intensity (F/F_0) of TPBT-ssDNA and TPBT-dsDNA mixture solution upon blue light illumination (460 nm, 25 mW cm^{-2}).

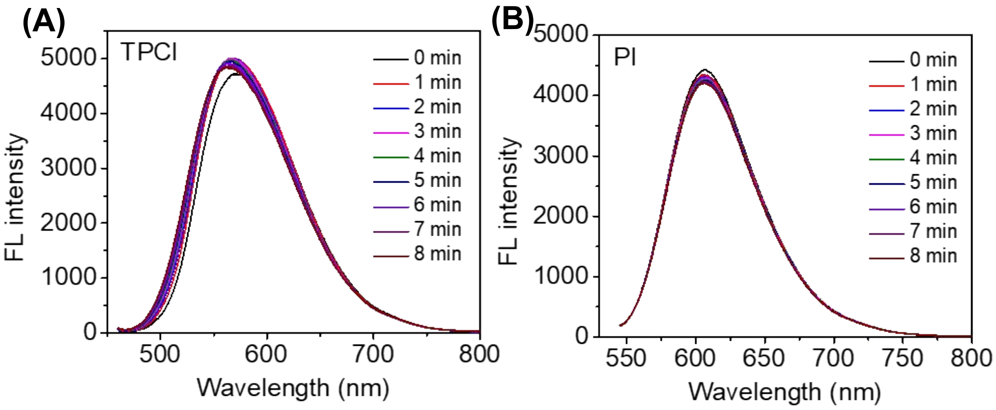

Figure S4 Fluorescence change of TPCI-DNA (A) and PI-DNA (B) complexes (DNA is excess) upon blue light illumination (460 nm, 25 mW cm^{-2})

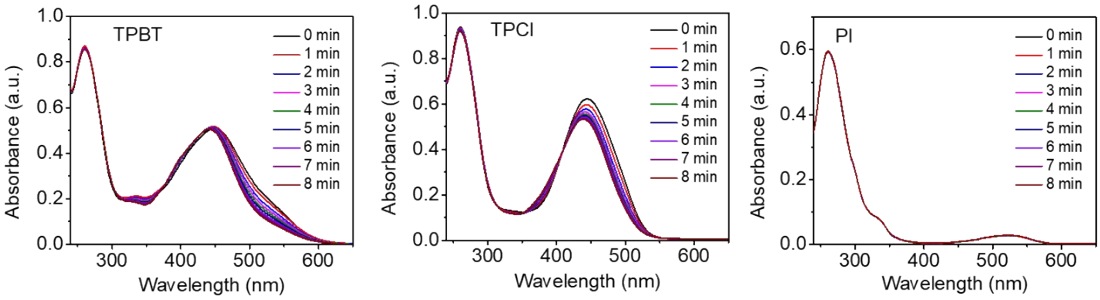

Figure S5 Corresponding absorption spectroscopic change of the TPBT, TPCI and PI in the presence of excess ctDNA upon light irradiation. (25 mW cm^{-2}, Dye = 10 μM).

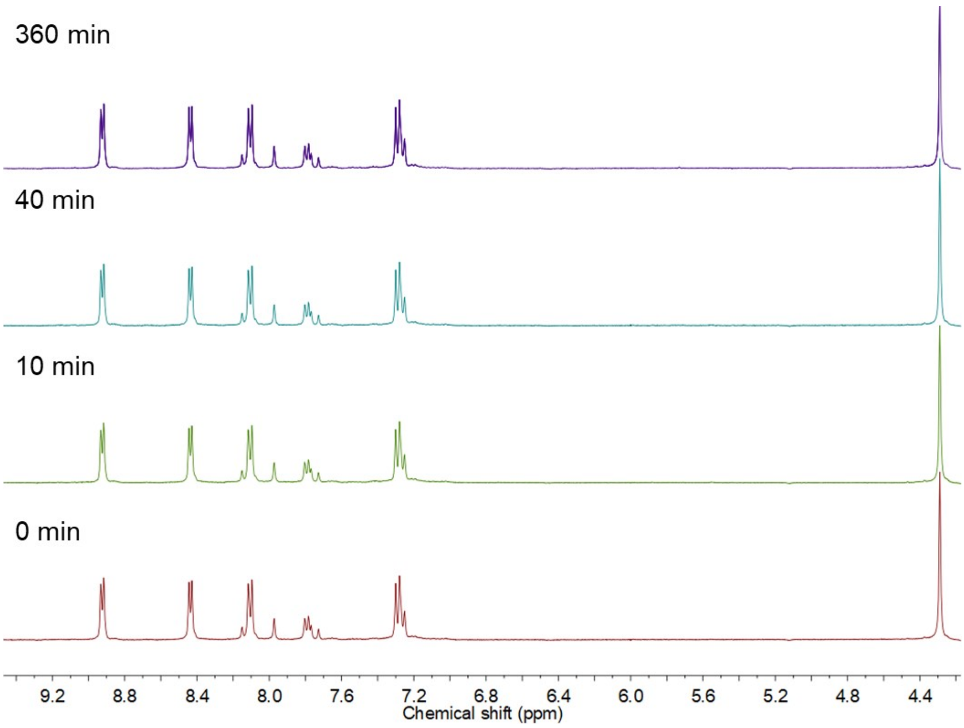

Figure S6 ^{1}H NMR spectra change of TPBT in DMSO-*d6* with various blue light irradiation time (460 nm, 25 mW cm^{-2}).

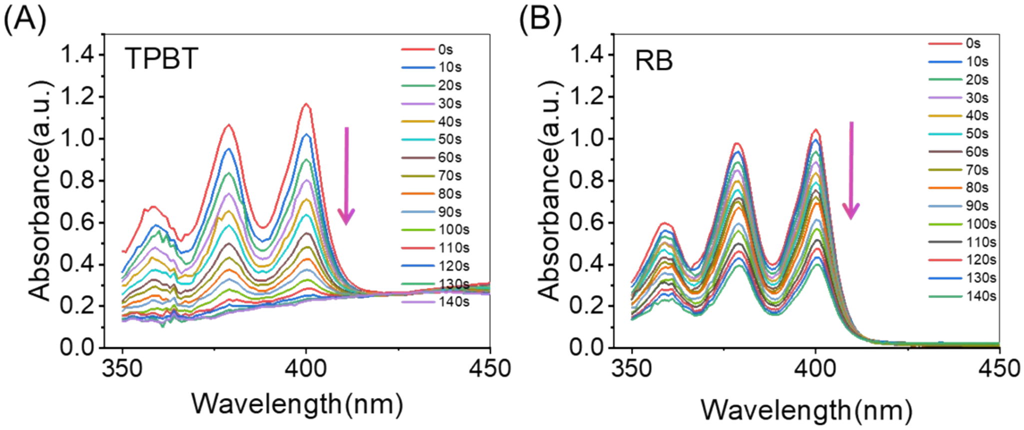

Figure S7 A) UV–vis absorption spectra of ABDA (100 μM) in TPBT and RB solution (5 μM) irradiated for different durations with white light irradiation (380-800 nm, 25 mW cm^{-2}).

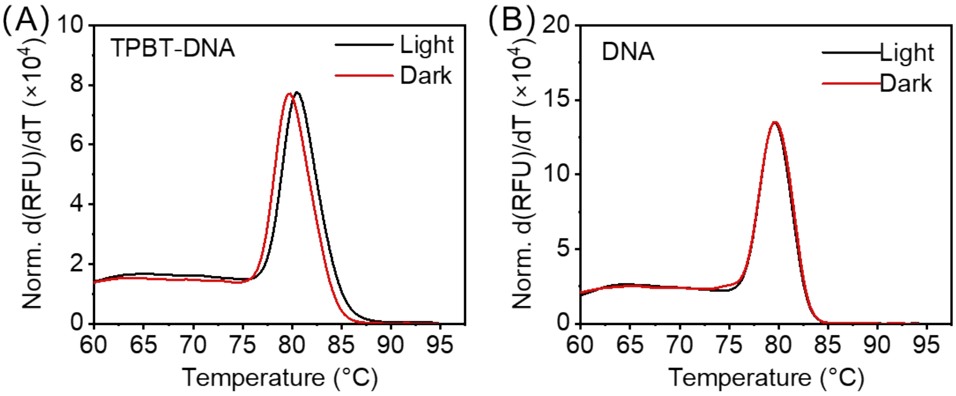

Figure S8 (A) Melting curves of double-stranded cDNA obtained after reverse transcription and second-strand synthesis, before and after light irradiation, monitored using SYBR® Green. (B) Melting curves of TPBT–cDNA complexes under identical conditions.

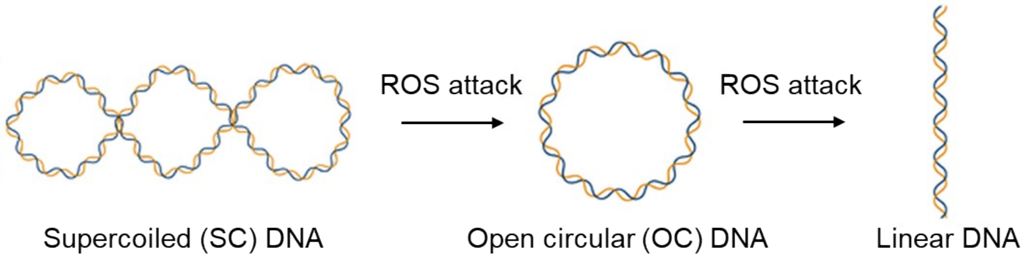

Figure S9 TPBT-generated ROS induce the conversion of plasmid DNA from supercoiled (SC) to open circular (OC) and linear forms.

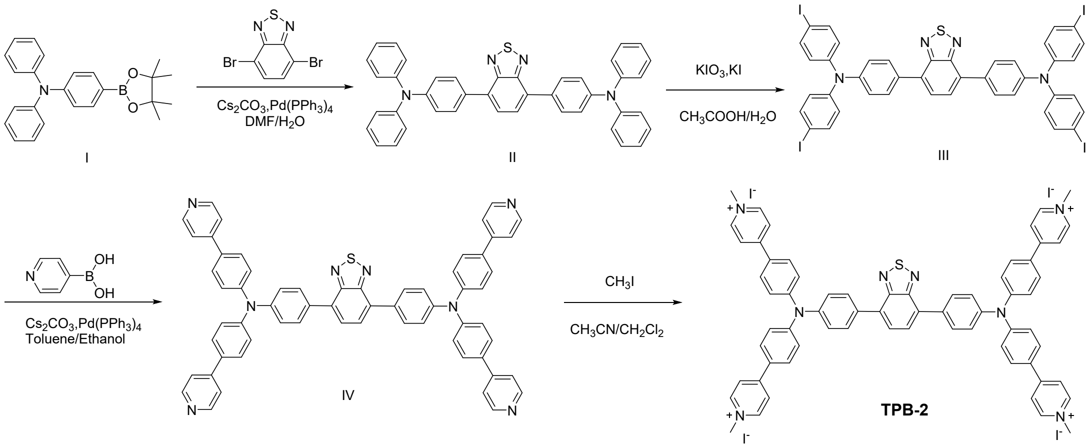

Figure S10 Synthetic routes to TPB-2.

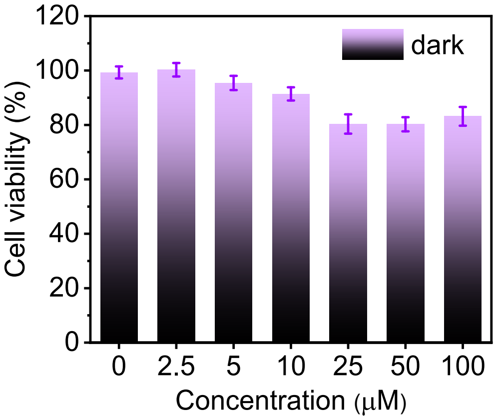

Figure S11 MTT assay of HeLa cancer cells pretreated with TPBT in different concentrations without light illumination.

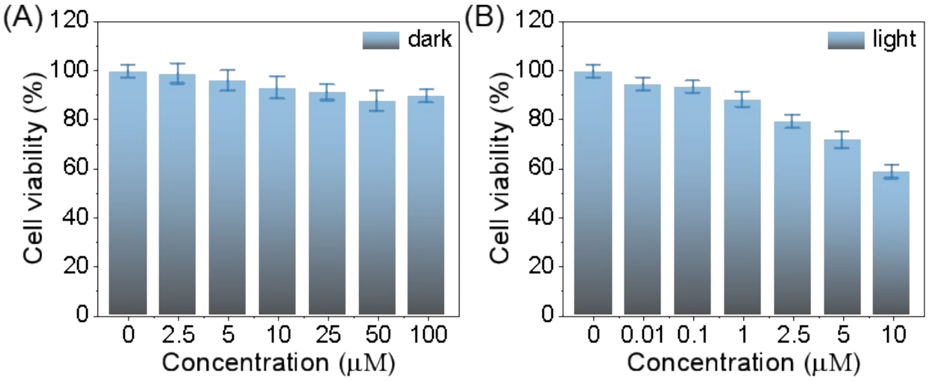

Figure S12 MTT assay of NIH 3T3 cells pretreated with TPBT in different concentrations in dark (A) or with (B) white light illumination (380–800 nm, 25mW cm^{-2}).

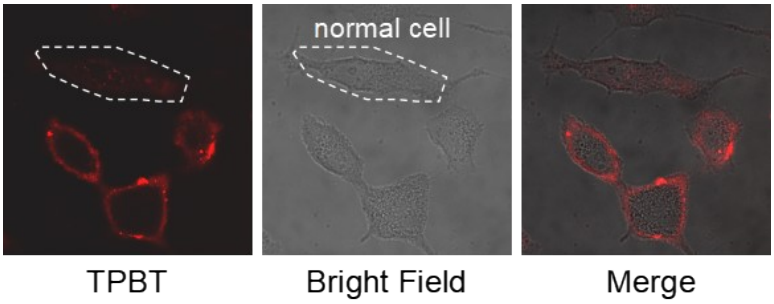

Figure S13 CLSM images of TPBT-pretreated NIH 3T3 and HeLa cells (CLSM excitation laser: λ_{ex} = 488 nm, 1% of laser power, signal collection at 600-700 nm for TPBT red channel).

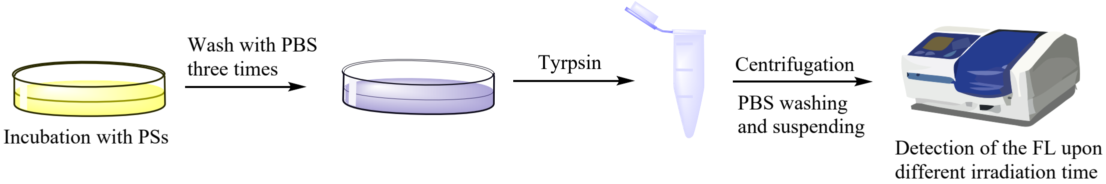

Figure S14 Procedures for photodynamic theranostics detection upon white light irradiation. The cells were incubated with PS solutions for 4h, then washed by PBS three times. After that, the cells were digested with trypsin and collected with three times washing. The suspending cells in cuvettes was then receiving the PDT, and their FL response was recorded by a FL spectrophotometer. [PS] = 10 μM.

Detection of the singlet oxygen ($^1O_2$) quantum yield:

The$^1O_2$ quantum yield of TPBT aqueous solution under white light irradiation was detected by utilizing 9,10-anthracenediyl-bis(methylene) dimalonic acid (ABDA) as ROS probe and Rose Bengal (RB) as a reference. The $^1O_2$ quantum yield was calculated using the following equation,

$$\Phi_{sample} = \Phi_{RB}\frac{K_{sample} \times A_{RB}}{K_{RB} \times A_{sample}} \quad (1)$$

The slope of the absorbance in relation to irradiation time is denoted as K, with A signifying the light absorbed by TPBT or RB across the white light spectra. The $^1O_2$ quantum yield of reference RB aqueous solution is 75%.Values of K_{TPBT} and K_{RB} have been computed as 0.01365 and 0.00642 (Figure S6), while the corresponding values for the spectral range of the white light from 380 nm to 800 nm (A_{TPBT} and A_{RB}) were 54.049 and 20.8725, respectively. Consequently, the $^1O_2$ quantum yield of TPBT (Φ_{TPBT}) aqueous solution has determined to be 62%.

The Synthetic of TPB-2:

The synthesis procedure of compound II. Under a nitrogen atmosphere, a mixture of N,N-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (2.40 g, 6.47 mmol), 4,7-dibromobenzo[c][1,2,5]thiadiazole (0.77 g, 2.62 mmol), Cs_2CO_3 (6.00 g, 18.41 mmol) and $Pd(PPh_3)_4$ (0.31 g, 0.27 mmol) in a mixture solvent of DMF (80 mL) and water (10 mL) was stirred and heated to 110°C for 12 h. The progress of the reaction was monitored by TLC. Then the solvent was removed under vacuum and the raw product was extracted three times by using dichloromethane (DCM) and water. The organic layers were combined and then the solvent was removed under reduced pressure, and the residue was purified by chromatography on a silica gel column with Hexane/DCM (v/v 10:1) to get compound *II.* (1.23 g, yield: 73%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.6 Hz, 4H), 7.67 (s, 2H), 7.22 (t, *J* = 7.8 Hz, 8H), 7.12 (m, 12H), 6.99 (t, *J* = 7.1 Hz, 4H).

The synthesis procedure of compound III. Under a nitrogen atmosphere, a mixture of 4,4'-(benzo[c][1,2,5]thiadiazole-4,7-diyl)bis(N,N-diphenylaniline) (0.49 g, 0.80 mmol), KI (0.40 g, 2.45 mmol) and KIO_3 (0.35 g, 1.67 mmol) in a mixture solvent of CH_3COOH (80 mL) and water (10 mL) was stirred and heated to 80°C for 10 h. The progress of the reaction was monitored by thin layer chromatography (TLC). The raw product was added to 500 mL of pure water. Then the solvent was removed under reduced pressure. Then the resulting product was dried in an oven at 80°C to dry the remaining solvent to get compound 3 (0.77 g, yield: 86%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 4H), 7.68 (s, 2H), 7.51 (d, *J* = 8.0 Hz, 8H), 7.13 (d, *J* = 7.8 Hz, 4H), 6.85 (d, *J* = 8.0 Hz, 8H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.82, 146.86, 138.45, 132.72, 130.23, 129.55, 126.34, 123.91, 86.47. **HRMS (ESI):** m/z calculated for $C_{42}H_{26}I_4N_4S$, 1126.806; found: 1126.815.

*The synthesis procedure of compound IV***.** Under a nitrogen atmosphere, a mixture of compound 2 (0.30 g, 0.26 mmol), $Pd(PPh_3)_4$ (0.03 g, 0.26 mmol) and Cs_2CO_3 (0.17 g, 0.53 mmol) in toluene (85 mL) was stirred and heated to 60°C, then a solution of pyridine-4-boronic acid (0.26 g, 2.13 mmol) in 20 mL ethanol was injected slowly. This mixture was stirred for 15 h at 100°C under an atmosphere of nitrogen. After cooling down to room temperature, the solvent was removed under reduced pressure. The raw product was extracted three times using DCM and water. The organic layers were combined and dried with anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure, and the residue was purified by chromatography on a silica gel column with DCM/ethanol (v/v 20:1) to get compound 4 as an orange red solid (0.10 g, yield: 26%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 5.8 Hz, 8H), 7.97 (d, *J* = 8.6 Hz, 4H), 7.79 (s, 2H), 7.59 (d, *J* = 8.6 Hz, 8H), 7.49 (d, *J* = 6.0 Hz, 8H), 7.31 (t, *J* = 8.8 Hz, 12H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.06, 150.19, 148.03, 147.48, 146.95, 132.58, 132.18, 130.31, 128.02, 127.69, 124.61, 121.02. **HRMS (ESI):** m/z calculated for $C_{62}H_{42}N_8S$, 931.325; found: 931.330.

The synthesis procedure of TPB-2. Under a nitrogen atmosphere, compound 3 (30 mg, 0.08 mmol) and methyl iodide (114 mg, 0.1 mL, 0.80 mmol) were dissolved in 20 mL acetonitrile. The mixture was stirred and heated to 40°C for 1 h and then refluxed for 12 h at 80°C. After cooling to room temperature, the mixture was poured into diethyl ether to get precipitates. The precipitates were then washed with diethyl ether three times and dried under reduced pressure to afford the product as an red powder (41 mg, yield: 80%), **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 8.89 (d, *J* = 6.5 Hz, 8H), 8.40 (d, *J* = 6.4 Hz, 8H), 8.10 (t, *J* = 9.3 Hz, 12H), 8.00 (s, 2H), 7.36 (d, *J* = 8.3 Hz, 4H), 7.29 (d, *J* = 8.5 Hz, 8H), 4.25 (s, 12H), **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 153.79, 153.56, 150.02, 145.84, 134.34, 131.75, 131.35, 130.29, 128.74, 128.19, 126.63, 124.22, 123.50, 47.36. **HRMS (ESI):** m/z calculated for $C_{42}H_{26}I_4N_4S^{4+}$, 247.604; found: 247.604.