Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Electronic Supplementary Information

Detection of cell-surface sialic acids and photodynamic eradication of cancer cells using dye-modified polydopamine-coated gold nanobipyramids

Yue Cao, Shenghua Han, Han Zhang, Jie Wang, Qiao-Yan Jiang, Yimin Zhou, You-Jia Yu, Jianfang Wang, Feng Chen* and Dennis K. P. Ng*

Experimental section

General. Toluene and CH_2Cl_2 were distilled from sodium and an INERT solvent purification system respectively. All other solvents and reagents were of reagent grade and used as received. All aqueous solutions were prepared using ultrapure water (18 MΩ, Milli-Q, Millipore). All the reactions were performed under an atmosphere of nitrogen. Chromatographic purification was performed on silica gel (Macherey-Nagel, 230-400 mesh) with the indicated eluents. Size-exclusion chromatography was performed on Bio-Beads S-X1 beads using tetrahydrofuran (THF) as the eluent. Compounds $\mathbf{1}^{R1}$ and $\mathbf{2}^{R2}$ were prepared as described.

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker Avance III 700 spectrometer (^1H, 700 MHz; ^{13}C, 176.0 MHz) in $CDCl_3$. Electrospray ionisation (ESI) mass spectra were recorded on a Q Exactive Focus Orbitrap mass spectrometer. UV-Vis absorption and steady-state fluorescence spectra were taken on a Shimazu UV-1800 UV-Vis spectrophotometer and a Hitachi F-7000 spectrofluorometer respectively. Transmission electron microscopy (TEM) images were obtained on a FEI Tecnai G2 Spirit transmission electron microscope operated at 120 keV acceleration voltage. The dark-field images were obtained by an inverted microscope (eclipse Ti-U, Nikon, Japan) equipped with a dark-field condenser ($0.8 < NA < 0.95$) and a 40× objective len ($NA = 0.8$), and a white light source (100 W halogen lamp) was used to excite the plasmon resonance scattering light of AuBPs. The fluorescence images were obtained on the same microscope using a mercury lamp (100 W Epi illuminator) as the excitation light source. Raman spectra were recorded on a Raman microspectrometer with an inverted microscope (Ti2-U, Nikon, Japan) and a Raman spectrograph (HRS-300S, TPI, USA). The system was equipped with a class IIIB laser product (785 nm, 80 mW), focusing on sample with a 60x objective len.

Preparation of 3

A mixture of BODIPY **1** (0.3 g, 0.6 mmol), benzaldehyde **2** (0.8 g, 3.0 mmol), piperidine (1.2 mL), acetic acid (1.0 mL) and a small amount of $Mg(ClO_4)_2$ in toluene (100 mL) was heated under reflux. The water formed during the reaction was removed azeotropically with a Dean-Stark apparatus. The reaction was monitored by thin-layer chromatography. After the reaction was completed, the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (75 mL) and the solution was washed with water (75 mL × 3). The solvent was then removed under reduced pressure and the residue was purified by column chromatography on silica gel using CH_2Cl_2/CH_3OH (100/1, v/v) as the eluent. The crude product was further purified by size-exclusion chromatography using THF as the eluent to give a green solid (0.3 g, 50%). ^{1}H NMR: δ 8.05 (d, *J* = 16.8 Hz, 2 H, C=CH), 7.55-7.58 (m, 6 H, C=CH and ArH), 7.07 (d, *J* = 8.4 Hz, 2 H, ArH), 6.94-6.96 (m, 6 H, ArH), 6.50 (s, 1 H, OH), 4.19 (t, *J* = 4.9 Hz, 4 H, OCH_2), 3.90 (t, *J* = 4.9 Hz, 4 H, OCH_2), 3.76-3.78 (m, 4 H, OCH_2), 3.70-3.72 (m, 4 H, OCH_2), 3.67-3.68 (m, 4 H, OCH_2), 3.57-3.58 (m, 4 H, OCH_2), 3.39 (s, 6 H, OCH_3), 1.40 (s, 6 H, CH_3). ^{13}C{^{1}H} NMR: δ 159.9, 157.2, 148.2, 141.1, 139.2, 138.5, 132.6, 130.1, 129.9, 129.4, 126.8, 116.5, 116.3, 115.0, 110.1, 72.0, 71.0, 70.8, 70.7, 69.8, 67.6, 59.2, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{47}H_{53}BBr_2F_2N_2NaO_9$ $[M+Na]^+$ 1021.2064, found 1021.2065.

Preparation of BDP

BODIPY **3** (0.15 g, 0.15 mmol) and 4-carboxyphenylboronic acid (**4**) (0.10 g, 0.60 mmol) were dissolved in CH_2Cl_2 (60 mL). EDC·HCl (115 mg, 0.60 mmol) and DMAP (73 mg, 0.60 mmol) were then added to the above solution. The mixture was stirred at room temperature for 48 h and then evaporated. The residue was dissolved in CH_2Cl_2 (75 mL) and the solution was washed with water (75 mL × 3). The solvent was removed under reduced pressure and the residue was purified

by column chromatography on silica gel using CH_2Cl_2/CH_3OH (30/1, v/v) as the eluent to give BDP as a green solid (35 mg, 20%). ^{1}H NMR: δ 8.08-8.13 (m, 4 H, C=CH and ArH), 7.85 (d, *J* = 7.7 Hz, 2 H, ArH), 7.62 (d, *J* = 16.8 Hz, 2 H, ArH), 7.56 (d, *J* = 8.4 Hz, 4 H, ArH), 7.35 (d, *J* = 8.4 Hz, 2 H, ArH), 7.20 (d, *J* = 8.4 Hz, 2 H, ArH), 6.91 (d, *J* = 8.4 Hz, 4 H, ArH), 4.18 (t, *J* = 4.9 Hz, 4 H, OCH_2), 3.90 (t, *J* = 4.9 Hz, 4 H, OCH_2), 3.78-3.80 (m, 4 H, OCH_2), 3.74-3.75 (m, 4 H, OCH_2), 3.70-3.71 (m, 4 H, OCH_2), 3.59-3.61 (m, 4 H, OCH_2), 3.41 (s, 6 H, OCH_3), 1.45 (s, 6 H, CH_3). ^{13}C{^{1}H} NMR: δ 165.0, 160.1, 152.0, 148.7, 141.2, 139.2, 137.8, 134.3, 132.2, 132.1, 130.8, 129.9, 129.5, 129.4, 129.3, 123.2, 116.1, 115.0, 110.4, 71.9, 70.8, 70.7, 70.6, 69.8, 67.5, 59.2, 14.1. HRMS (ESI): *m*/*z* calcd for $C_{54}H_{58}B_2Br_2F_2N_2NaO_{12}$ $[M+Na]^+$ 1169.2406, found 1169.2412.

Determination of fluorescence quantum yield

The fluorescence quantum yield (Φ_F) of BDP (in DMF) was determined by the equation:[R3]

$$\Phi_{F(sample)} = \left(\frac{F_{sample}}{F_{ref}}\right)\left(\frac{A_{ref}}{A_{sample}}\right)\left(\frac{n^2_{sample}}{n^2_{ref}}\right)\Phi_{F(ref)}$$

where *F*, *A* and *n* are the measured fluorescence (area under the emission peak), the absorbance at the excitation wavelength (610 nm) and the refractive index of the solvent. The unsubstituted zinc(II) phthalocyanine (ZnPc) in DMF was used as the reference [$\Phi_{F(ref)} = 0.28$].[R4]

Determination of singlet oxygen quantum yield

Mixtures of 1,3-diphenylisobenzofuran (DPBF) (30 μM) and BDP or ZnPc **(**2 μM**)** in DMF were prepared in the dark and then irradiated with red light coming from a 100 W halogen lamp after passing through a water tank for cooling and a colour glass filter (Newport, cut-on at 610 nm). The

absorbance of DPBF at 415 nm was recorded immediately after irradiation for every 5 sec. The rate of decay of DPBF was monitored over a total irradiation time of 60 sec. The singlet oxygen quantum yield of BDP (in DMF) was determined by the equation:[R5]

$$\Phi_{\Delta(\text{sample})} = \left(\frac{W^{sample}\, I_{abs}^{ref}}{W^{ref}\, I_{abs}^{sample}}\right)\Phi_{\Delta}^{ref}$$

where W and I_{abs} are the photobleaching rate of DPBF and the rate of light absorption respectively. ZnPc in DMF was used as the reference [$\Phi_{F(ref)} = 0.56$].[R6]

Preparation of gold nanobipyramids

Growth of AuBPs： A freshly prepared ice-cooled $NaBH_4$ solution (0.01 M, 0.15 mL) was added under vigorous stirring into an aqueous mixture of $HAuCl_4$ (0.01 M, 0.125 mL), trisodium citrate (0.01 M, 0.25 mL) and water (9.625 mL). The resulting seed solution was kept at room temperature for 2 h before use. This seed solution (0.2 mL) was then injected into the growth solution prepared by mixing cetyltrimethylammonium bromide (CTAB) (0.1 M, 40 mL), $HAuCl_4$ (0.01 M, 2 mL), $AgNO_3$ (0.01 M, 0.4 mL), HCl (1 M, 0.8 mL) and ascorbic acid (0.1 M, 0.32 mL) in deionised water, followed by gentle inversion mixing for 10 s. The mixture was left undisturbed overnight at room temperature. The longitudinal plasmon wavelength of the obtained AuBP sample was found to be *ca.* 800 nm.

Purification of AuBPs： This AuBP suspension (40 mL) was then centrifuged at 6800 rpm for 10 min. The precipitate was redispersed in a CTAB solution (0.08 M, 30 mL), which was then mixed with $AgNO_3$ (0.01 M, 8 mL) and ascorbic acid (0.1 M, 4 mL). The resulting mixture was kept in an oven at 60 ^{o}C for 4.5 h, during which Ag was overgrown on the Au nanocrystals to produce a bimetallic Au/Ag product. The volume of the $AgNO_3$ solution added into the AuBP solution could

be varied from 6 to 10 mL. The bimetallic Au/Ag product was then centrifuged at 5000 rpm for 10 min. The precipitate was redispersed in CTAB (0.05 M, 30 mL) and left undisturbed for *ca.* 4 h at 30 ^{o}C, during which the Au/Ag heteronanorods agglomerated together and precipitated on the bottom of the container, while the spherical (Au core)@(Ag shell) nanoparticles remained in the supernatant. The supernatant was discarded. The remaining Au/Ag heteronanorods were redispersed in water (20 mL). The resulting solution was subsequently mixed gently with $NH_3 \cdot H_2O$ (30 wt%, 0.8 mL) and H_2O_2 (1 M, 0.8 mL) and the mixture was kept undisturbed for 4 h. During this process, the Ag segments were gradually etched away. AgCl precipitate was seen to form on the bottom. The clear supernatant was carefully taken out and centrifuged at *ca.* 5000 rpm for 10 min. The product was redispersed in a CTAB solution (0.05 M, 10 mL) or water for further use. Based on the TEM images, the percentage of AuBPs in the purified product was found to be 99%.

Preparation of AuBP@PDA@BDP

The above AuBP suspension (1 mL) was added into a Tris buffer (10 mM, 1 mL) containing dopamine (0.05 mg mL^{-1}). The mixture was gently stirred at room temperature for 6 h. The AuBP@PDA nanoparticles formed were separated by centrifugation and redissolved in phosphate-buffered saline (PBS) (1 mL). For further surface modification with BDP, this AuBP@PDA suspension (500 μL) was mixed with a solution of BDP in PBS with 0.5% Tween 80 (3.4 μM, 500 μL). The mixture was stirred at room temperature for 12 h, followed by centrifugation and washing with deionised water twice. The resulting AuBP@PDA@BDP was dispersed in deionised water (1 mL) and stored at 4 ^{o}C for further use.

Density functional theory calculations

DFT calculations were performed using the Gauss View 5.0[R7] suite of programme at the level of B3LYP/6-311++g (3df, 2p) to simulate the Raman spectra of AuBP@PDA@BDP. Regarding the effect of the aqueous environment, the integral equation formalism version of polarisable continuum model (IEF-PCM)[R8] implemented in Gauss View 5.0 was included for the geometry optimisation and the vibrational frequency calculations of the most stable geometry. The Raman shifts were achieved based on all the calculated vibrational frequencies which were scaled by a factor of 0.967[R9] according to the utilised functional and basis set. The vibrational modes corresponding to the calculated peaks were subsequently analysed.

Cell lines and culture conditions

MCF-7 and Huh7 cells were maintained in Dulbecco's Modified Eagle Medium (DMEM) (ThermoFisher Scientific, cat. no. 12100-046) supplemented with fetal bovine serum (FBS) (10%, Invitrogen, cat. no. 10270-106) and penicillin-streptomycin (100 units mL^{-1} and 100 μg mL^{-1} respectively). The cells were grown at 37 °C in a humidified 5% CO_2 atmosphere.

Confocal fluorescence microscopy studies

Approximately 1 × 10^6 MCF-7 cells in DMEM (0.5 mL) were seeded on a confocal dish and incubated overnight at 37 °C with 5% CO_2. AuBP@PDA@BDP (100 μL) at different concentrations was then added into each cell-adhered dish for incubation at 37 ℃ for different periods of time. The cells were examined with an inverted microscope with an external triple channel optical system for confocal imaging.

Photocytotoxicity assay

The cytotoxicity of AuBP@PDA@BDP and BDP against MCF-7 cells was examined by MTT assay.[R10] Approximately 3×10^5 MCF-7 cells in DMEM were inoculated per well in 96-multiwell plates and incubated overnight at 37 ^oC in a humidified 5% CO_2 atmosphere. The photosensitisers

were diluted to respective concentrations with the culture medium. The cells were incubated with 100 μL of these probe solutions for 12 h at 37 °C under 5% CO_2. The cells were then rinsed with PBS and refed with 100 μL of the culture medium before being illuminated at ambient temperature. The light source consisted of a 300 W halogen lamp, a water tank for cooling and a colour glass filter (Newport) cut on at $\lambda = 610$ nm. The fluence rate ($\lambda \geq 610$ nm) was 40 mW cm^{-2}. Illumination of 20 min led to a total fluence of 48 J cm^{-2}. After illumination, the cells were incubated at 37 °C under 5% CO_2 overnight. The medium was discarded, and a fresh medium (50 μL) containing MTT (0.5 mg mL^{-1}) was added to each well, followed by incubation for 4 h under the same environment. The medium was removed, and the purple formazan crystals were dissolved with dimethyl sulfoxide (DMSO) (100 μL). The absorbance at 540 nm was measured using a Bio-Rad microplate reader. The average absorbance of the blank wells, which did not contain the cells, was subtracted from the readings of other wells. The relative cell viability (%) was calculated by [Σ ($A_{test}/A_{control} \times 100$)]/n, where A_{test} is the absorbance of the i^{th} datum (i = 1, 2, ..., n), $A_{control}$ is the average absorbance of control wells in which the photosensitiser was absent, and n (= 5) is the number of data points.

CCK-8 assay and EdU incorporation assay

The cell viability for Huh7 cells was assessed using the cell counting kit-8 (CCK-8, Dojindo). Cell proliferation was further determined by incorporation of 5-ethynyl-2'-deoxyuridine (EdU) with a EdU cell proliferation assay kit (RiboBio). Briefly, 4×10^4 Huh7 cells were seeded per well in a 24-well plate and left to adhere for 12 h. Culture medium with or without AuBP@PDA@BDP (0.24 nM) was added, and then the cells were incubated for 8 h. The cells were then rinsed with fresh medium before being illuminated using the above-mentioned light source for 20 min. After 12 h, the culture media were replaced with a fresh medium containing 50 μM EdU. After incubation for

4 h, the cells were washed twice with PBS and fixed using 4% (w/v) paraformaldehyde in PBS. The analysis was then conducted according to the manufacturer's protocol. The images were obtained on a EVOS cell imaging system (Life Technologies) automatically with 8-10 frames taken per well. The images were analysed using the Image J analysis software.

TUNEL assay

Cell apoptosis was studied using a TUNEL FITC apoptosis detection kit (Vazyme). In brief, 1×10^5 Huh7 cells were seeded per well in a 24-well plate and left to adhere for 12 h. Culture medium with or without AuBP@PDA@BDP (0.24 nM) was added, and then the cells were incubated for 8 h. After replacing the medium with a fresh medium, the cells were illuminated for 20 min using the light source described above. After 12 h, the cells were washed twice with PBS and fixed using 4% (w/v) paraformaldehyde in PBS. The analysis was then conducted according to the manufacturer's protocol. The images were obtained on a EVOS cell imaging system (Life Technologies) automatically with 8-10 frames taken per well. The images were analysed using the Image J analysis software.

Western blotting and antibodies

Proteins were extracted from Huh7 cells using RIPA lysis buffer, and the protein levels were analysed *via* Western blotting as described previously.[R11] The antibodies used for Western blotting were obtained as follows: anti-Bcl2 antibody (ProteinTech; 12789-1-AP, 1:1000), anti-Bax antibody (Bioworld; BS61098, 1:1000), anti-tubulin antibody (Bioworld; BS1482M, 1:5000), anti-cleaved caspase-3 antibody (Cell Signaling Technology; #9661, 1:1000), anti-PCNA antibody (Cell Signaling Technology; #2586S, 1:1000) and anti-Ki67 antibody (Beyotime; AF1738,

1:1000). Protein levels were normalised to tubulin.

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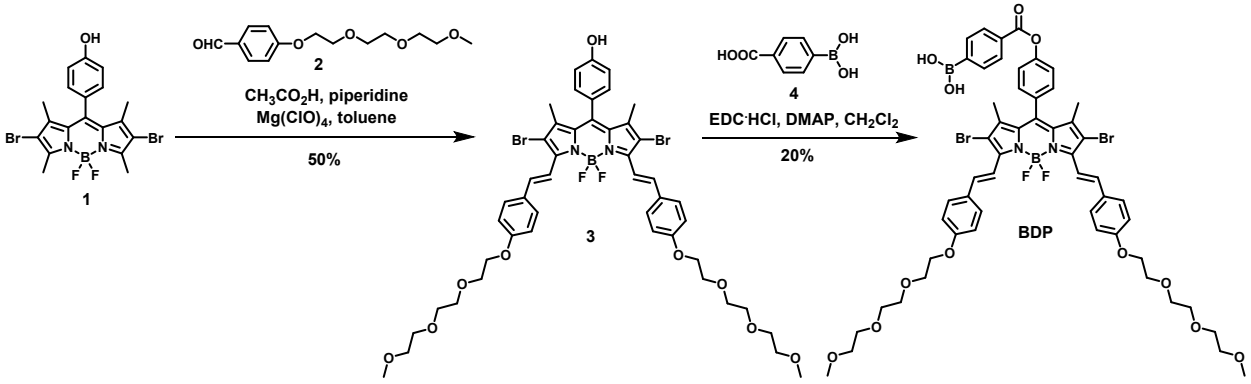

Scheme S1. Synthetic route for BDP.

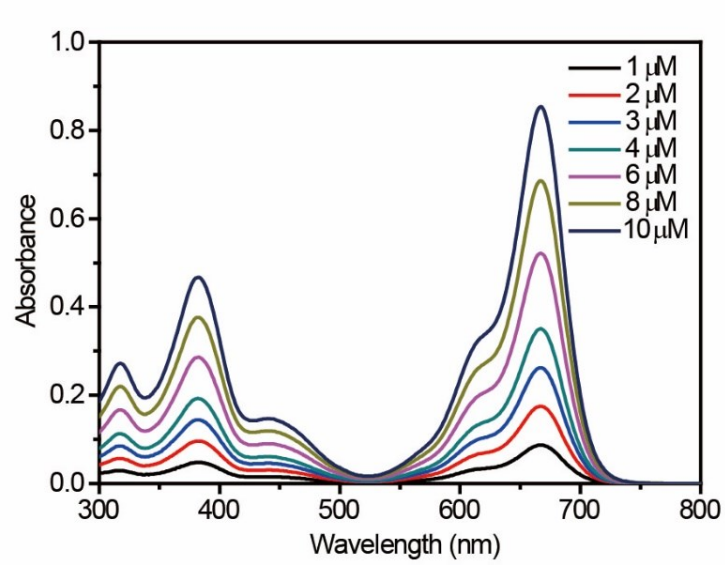

Fig. S1. UV-Vis spectra of BDP in DMF at different concentrations.

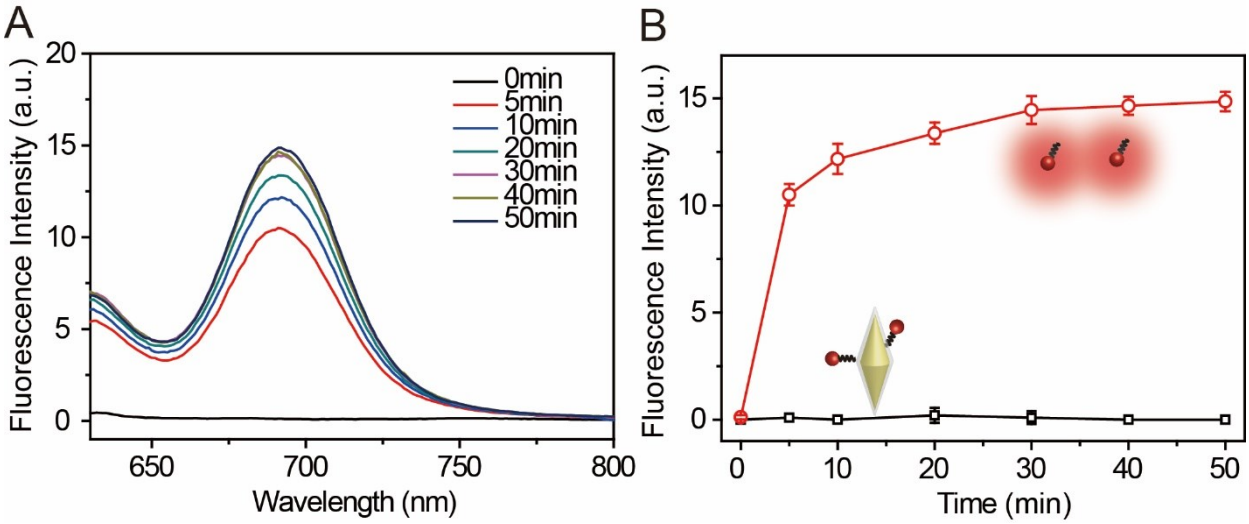

Fig. S2. (A) Change in fluorescence spectrum of AuBP@PDA@BDP ([AuBP] = 2.4 nM) in the presence of SA (0.1 μM) in PBS with time. (B) Plot of the fluorescence intensity versus the incubation time in the presence (red line) or absence (black line) of SA.

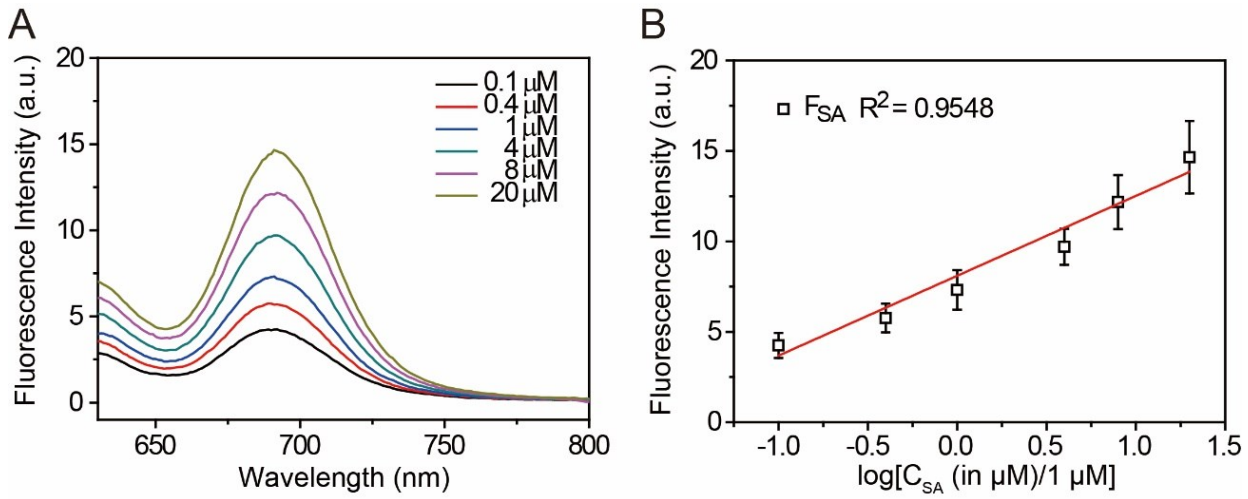

Fig. S3. (A) Change in fluorescence spectrum of AuBP@PDA@BDP ([AuBP] = 2.4 nM) with the concentration of SA in PBS. (B) Plot of the fluorescence intensity versus the logarithmic SA concentration.

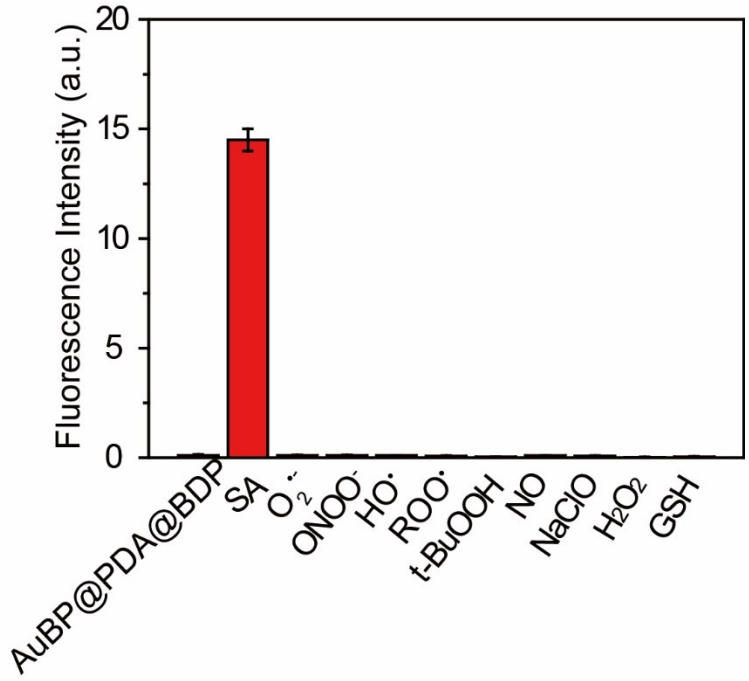

Fig. S4. Fluorescence intensities of AuBP@PDA@BDP ([AuBP] = 2.4 nM) in the presence of various biological species (0.1 μM) in PBS.

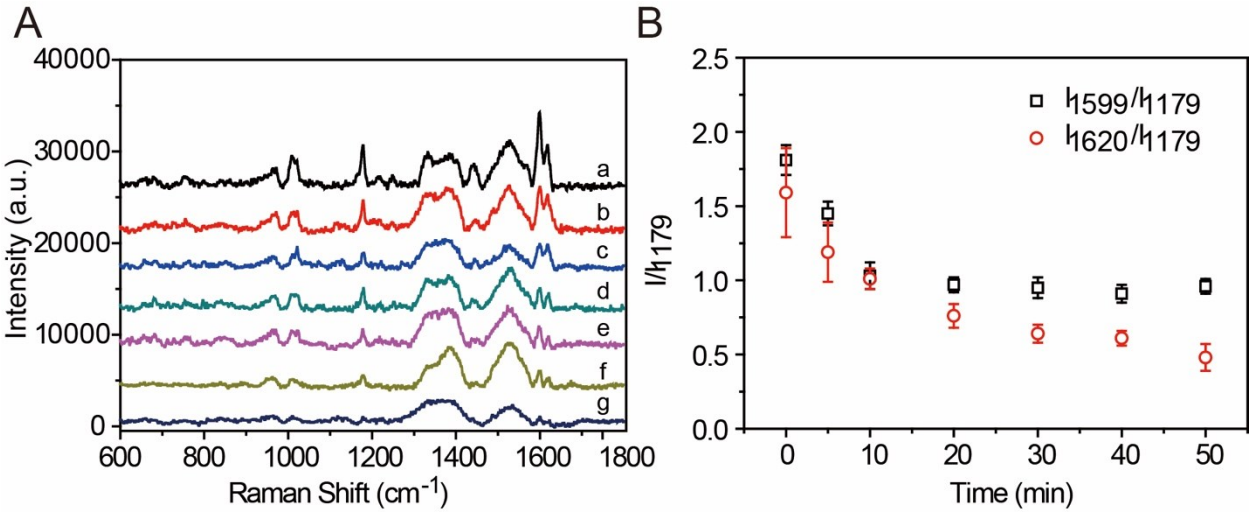

Fig. S5. (A) SERS spectra of AuBP@PDA@BDP ([AuBP] = 2.4 nM) upon treatment with a solution of SA (0.1 μM) in PBS for different period of time: (a) 0 min, (b) 5 min, (c) 10 min, (d) 20 min, (e) 30 min, (f) 40 min and (g) 50 min. (B) Plot of the ratiometric intensities of I_{1599}/I_{1179} and I_{1620}/I_{1179} versus the incubation time.

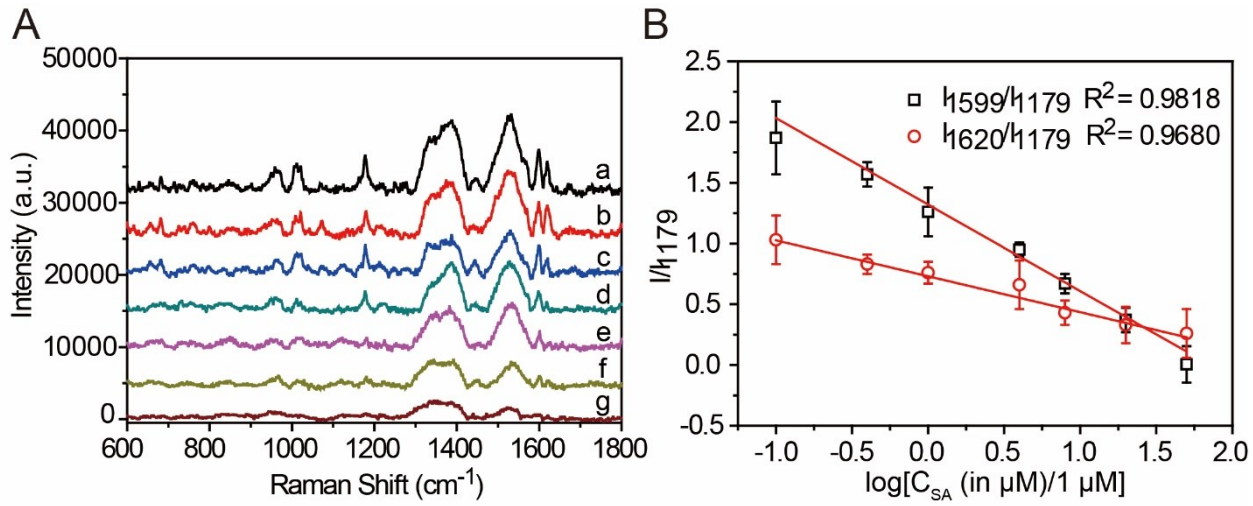

Fig. S6. (A) SERS spectra of AuBP@PDA@BDP ([AuBP] = 2.4 nM) upon treatment with various concentrations of SA in PBS: (a) 0.1 μM, (b) 0.4 μM, (c) 1 μM, (d) 4 μM, (e) 8 μM, (f) 15 μM and (g) 20 μM. (B) Plots of the ratiometric intensities of I_{1599}/I_{1179} and I_{1620}/I_{1179} versus the values of $\log[C_{SA}$ (in μM)/1 μM].

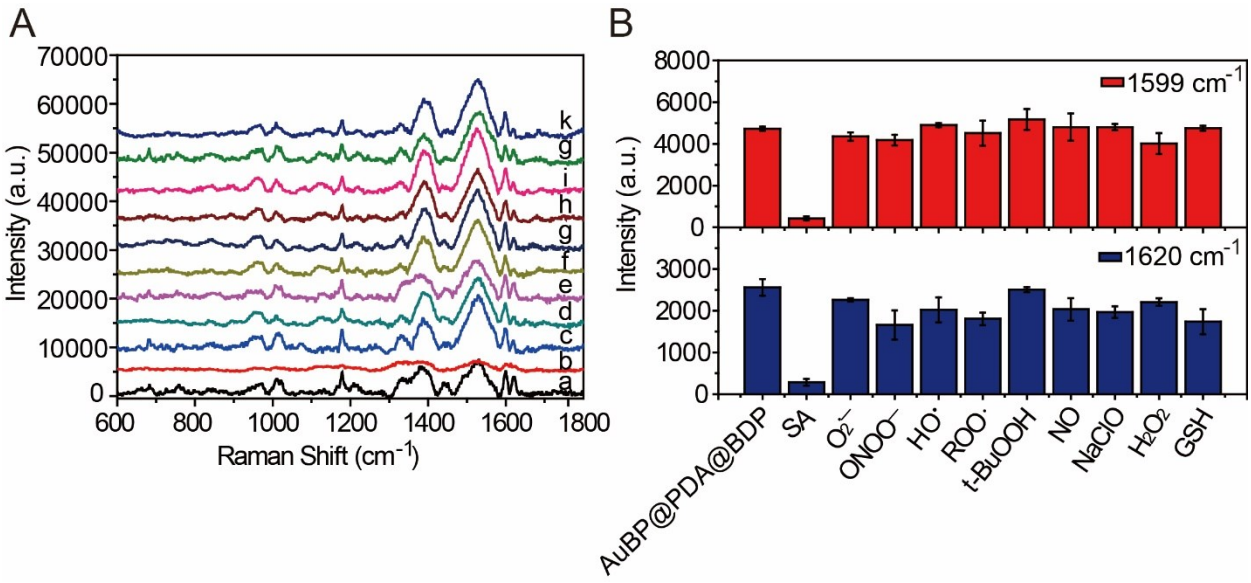

Fig. S7. (A) SERS spectra of AuBP@PDA@BDP ([AuBP] = 2.4 nM) upon treatment with various biological species (0.1 μM) in PBS: (a) without any biological species, (b) SA, (c) $O_2^{\bullet-}$, (d) $ONOO^-$, (e) $HO^{\bullet}$, (f) $ROO^{\bullet}$, (g) t-BuOOH, (h) NO, (i) NaClO, (j) H_2O_2 and (k) GSH. (B) The SERS intensities of AuBP@PDA@BDP at 1599 and 1620 cm^{-1} taken from the spectra in figure A.

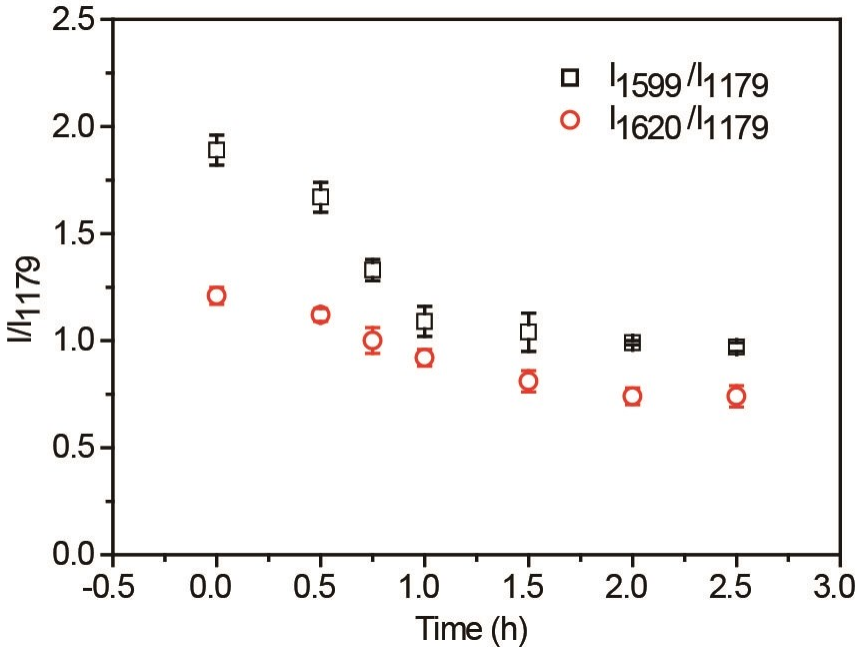

Fig. S8. Plots of the ratiometric Raman intensities of I_{1599}/I_{1179} and I_{1620}/I_{1179} versus the incubation time for AuBP@PDA@BDP-treated MCF-7 cells in the presence of SA (0.1 μM).

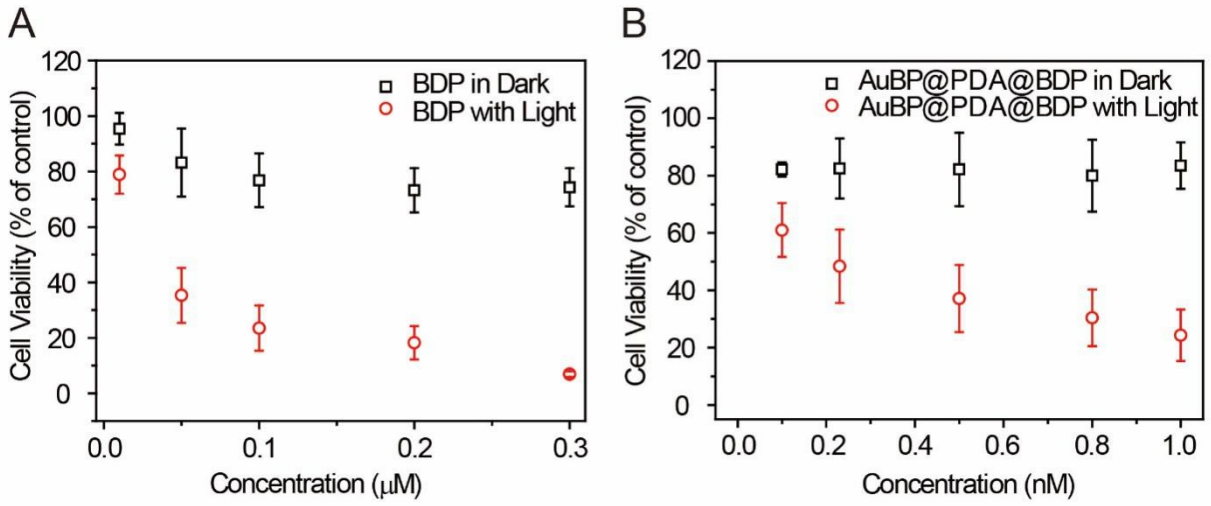

Fig. S9. Cytotoxicity of (A) BDP and (B) AuBP@PDA@BDP against MCF-7 cells both in the absence and presence of light (λ > 610 nm, 40 mW cm^{-2}, 48 J cm^{-2}). Data are expressed as the mean ± standard error of the mean of three independent experiments, each performed in quadruplicate.

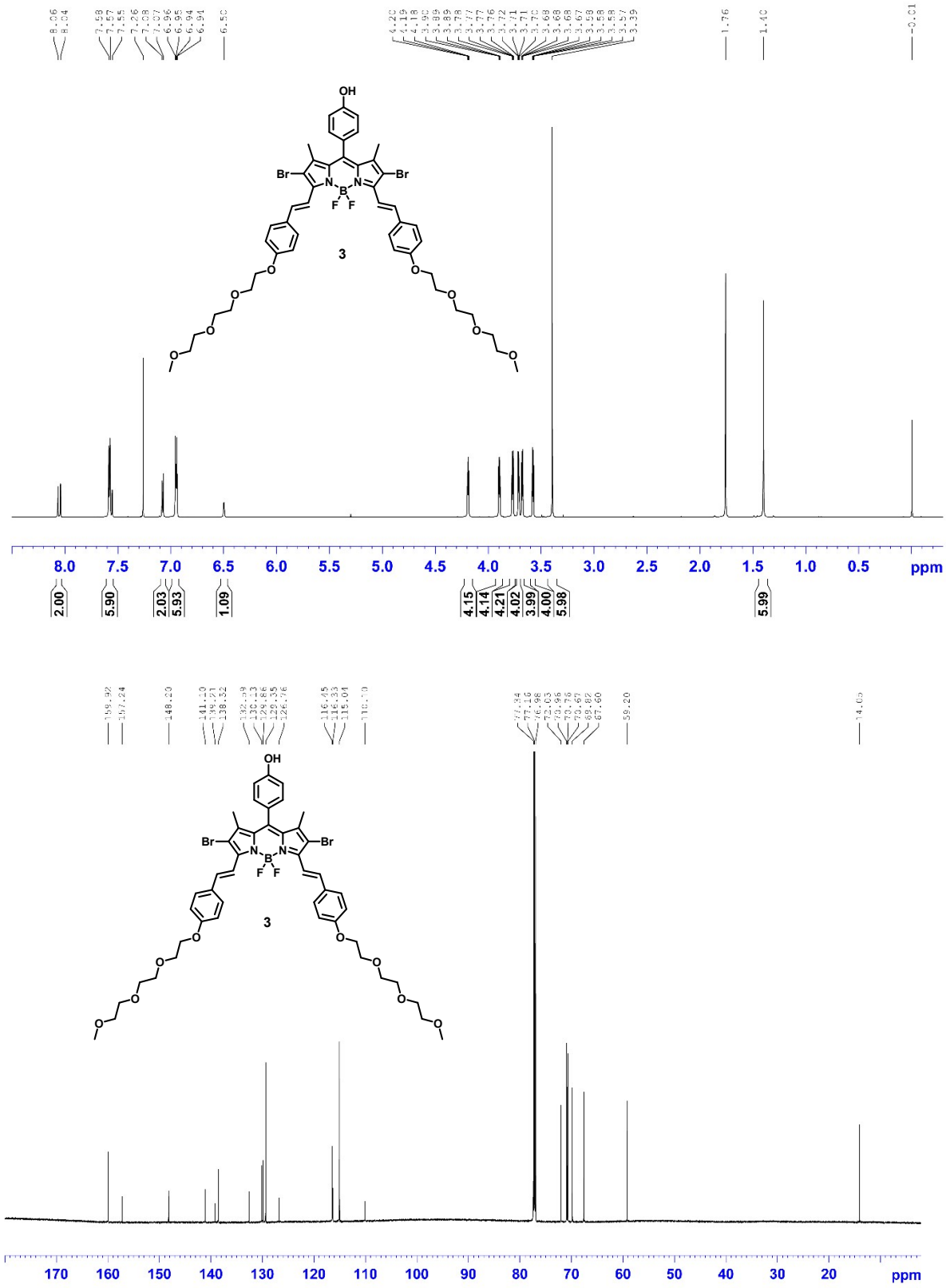

Fig. S10. ^{1}H (top) and $^{13}C\{^{1}H\}$ (bottom) NMR spectra of **3** in $CDCl_3$.

Thermo QEFMS Analysis Report

Analysis Info

Sample Name :	dsBDP-OH	Reference No.:	Qkpn043
Instrument :	Q Exactive Focus Orbitrap		
Source :	HESI II	Polarity :	Positive
Comment :	ESI pos, 3.5kV, by LC, with sheath gas		

Accurate Mass Measurement

Molecular formula :	($_{47}H_{53}BF_2Br_2N_2O_3$
Experimental Mass $[M+Na]^5$	1021.20651
Theoretical Mass $[M+Na]^5$	1021.20641
Error (ppm) :	0.0

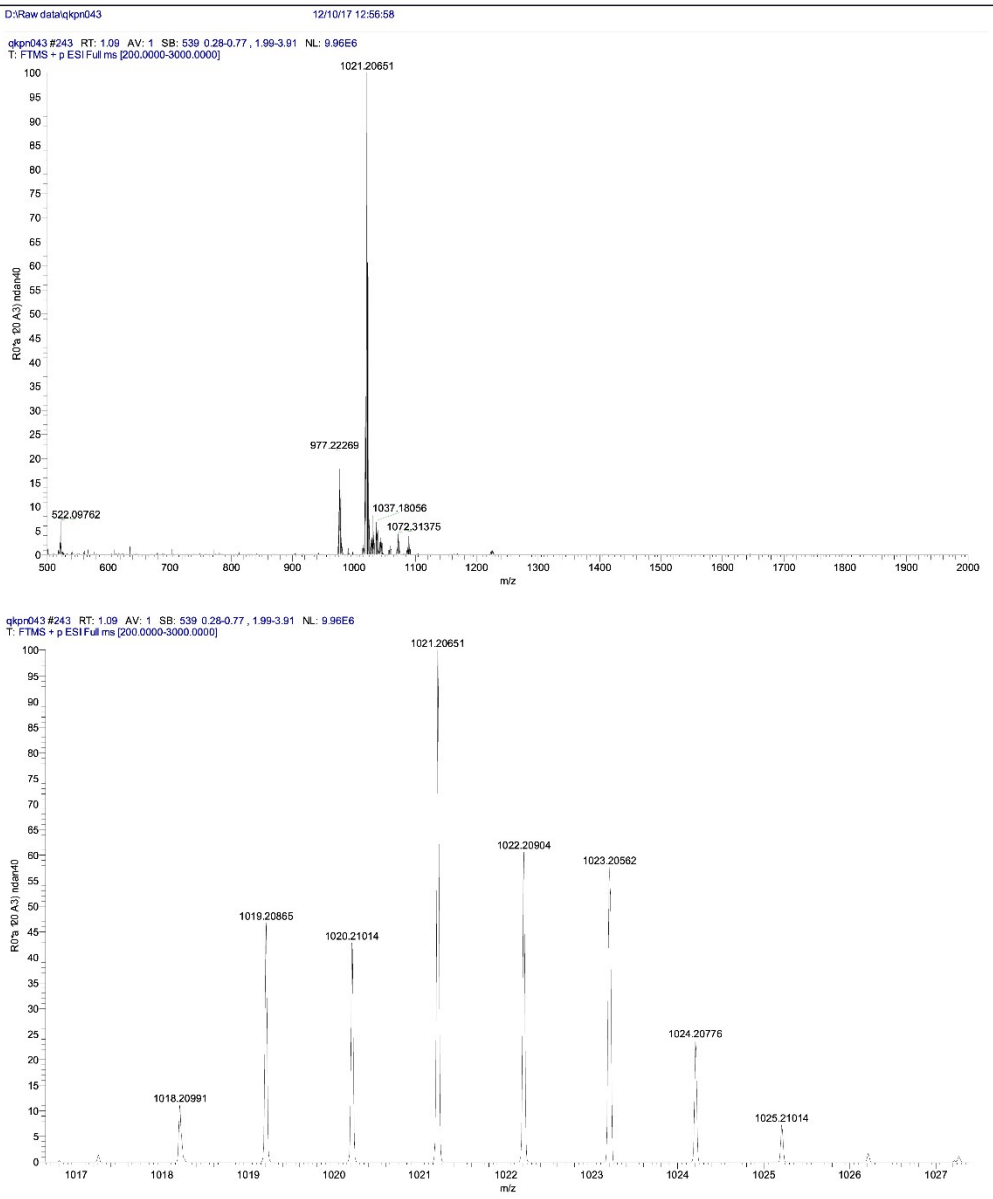

Fig. S11. ESI mass spectrum of **3**.

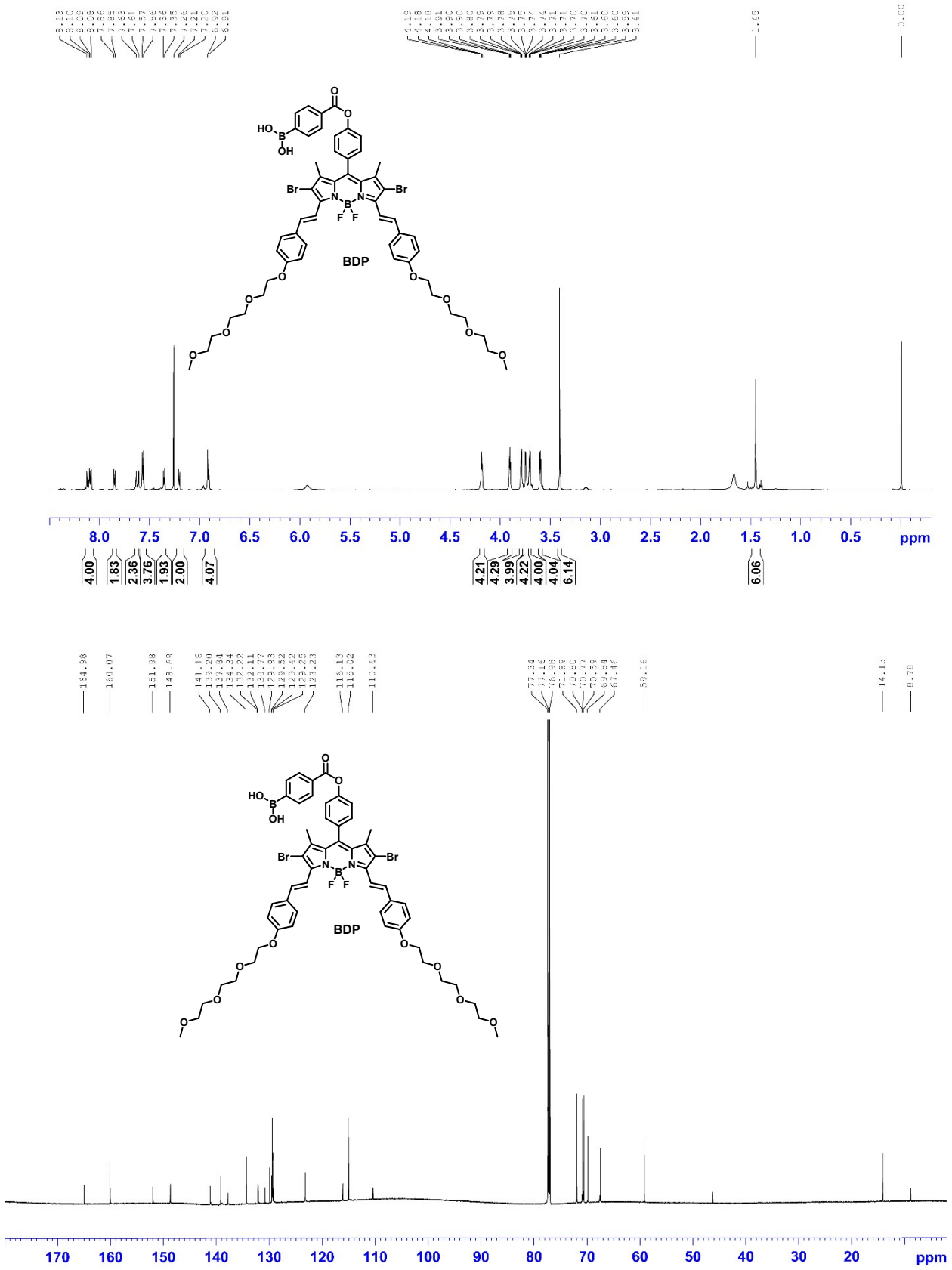

Fig. S12. ^{1}H (top) and $^{13}C\{^{1}H\}$ (bottom) NMR spectra of BDP in $CDCl_3$.

Thermo QEFMS Analysis Report

Analysis Info

Sample Name :	dsBDP-boronic acid	Reference No.:	Qkpn042
Instrument :	Q Exactive Focus Orbitrap		
Source :	HESI II	Polarity :	Positive
Comment :	ESI pos, 3.5kV, by LC, with sheath gas		

Accurate Mass Measurement

Molecular formula :	($_{54}$&$_{+2}$B$_2$$$_2Br_2N_2$%$_{12}$
Experimental Mass [M+Na]^5	1169.24117
Theoretical Mass [M+Na]^5	1169.24063
Error (ppm) :	0.4

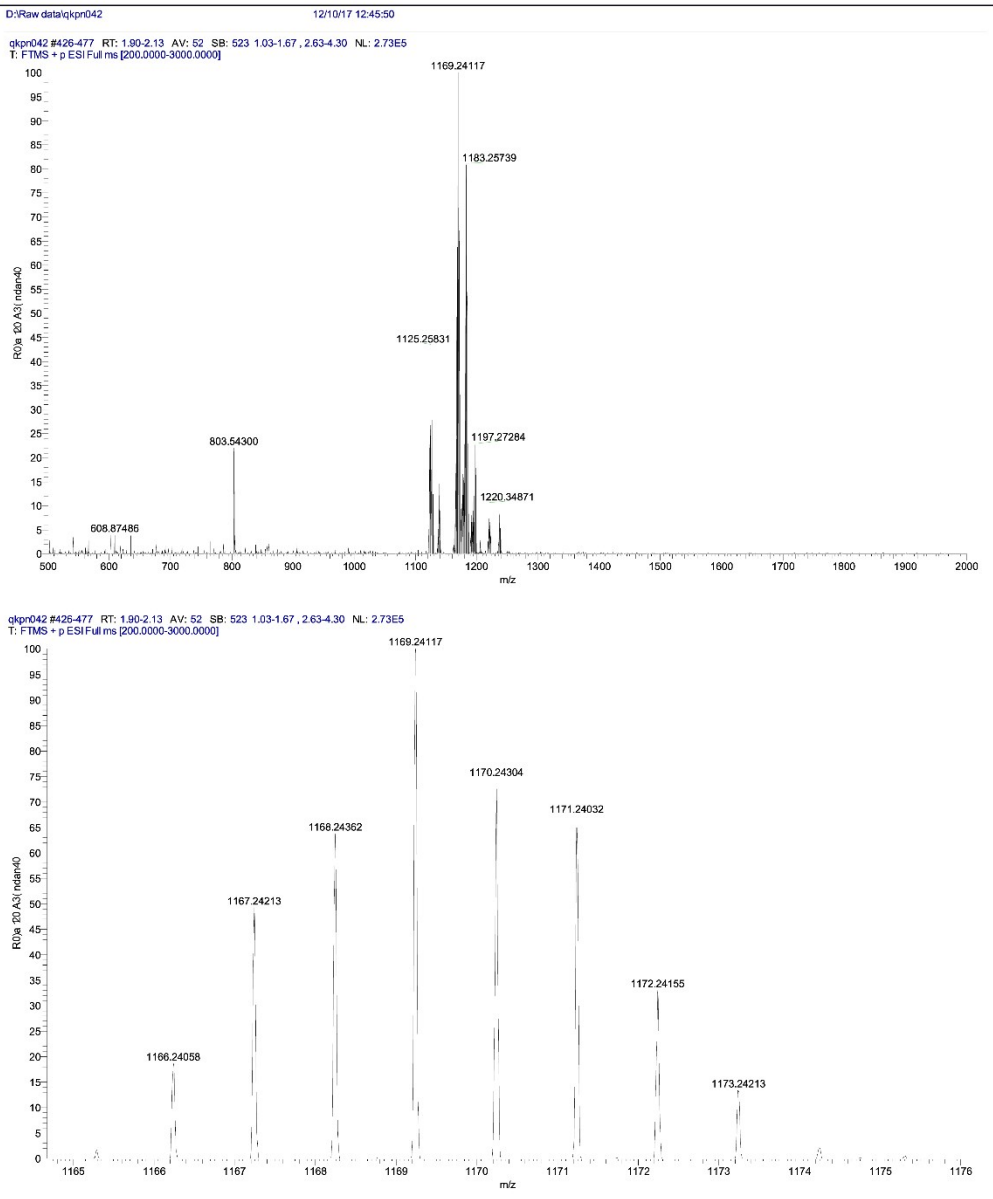

Fig. S13. ESI mass spectrum of BDP.

Table S1. Experimental and calculated SERS bands of AuBP@PDA@BDP and the corresponding assignments.

Experimental value (cm^{-1})	Calculated value (cm^{-1})	Assignment
972	988	C-O-C stretch
998	1011	Ar(C-C) stretch
	1069	Ar in-plane bending, CH_3 rock
1179	1167	N-B-N stretch, Ar(C-H) rock
1330	1321	Ar(C-N) rock, C-C stretch
1349	1352	Ar(C-C) asymmetric stretch, C-H rock
1378	1378	C-H rock
1389	1397	C-C stretch, C-H rock
1442	1454	B-OH rock
	1465	Ar(C-C) stretch, C-H rock
1529	1523	Ar(C-H) rock
1570	1589	C=C stretch
1599	1596	CH_2 rock
1620	1634	Ar(C-C) stretch
	1734	C=O rock