Small Water Soluble Pyrimidine Hexafluorophosphate Derivatives with High Two-Photon Absorption Activities in Near-IR Region and Their Biological Applications

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Synthesis and characterization

The synthetic routes for all the chromophores (6P to 10P) were illustrated in Scheme S1 and Scheme S2. Through the Solvent-free Wittig reaction, EX-6 to EX-10 was obtained in high yields[1]. The structures of twelve chromophores were characterized by IR, ^{1}H NMR, ^{13}C NMR spectra and elemental analyses.

Materials and Apparatus

All chemicals and solvents were dried and purified by usual methods. IR spectra (4000–400 cm^{-1}), as KBr pellets, were recorded on a Nicolet FT–IR 170 SX spectrophotometer. Mass spectra were obtained on a Micromass GCT-MS Spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 400 spectrometer with tms as internal standard.

Computational studies

To better understand the charge transfer state, density functional theory (DFT) calculations on all the compounds were carried out in vacuo. Optimizations were carried out with B3LYP(6-31G(d) without any symmetry restraint[2]. The time-dependent density functional theory (TD-DFT) {B3LYP(6-31G(d)} calculations, including optimizations and TD-DFT, were implemented with the G03 software[3]. Geometry optimization of singlet-singlet excitation energies were carried out with a basis set composed of 6-31G(d) for C, N, O and H atoms. The basis set was downloaded from the EMSL basis set library. The lowest 25 spin-allowed singlet-singlet transitions, up to energy of about 5 eV, were taken into account in the calculation of the absorption spectra.

Optical Measurements

The OPA spectra were measured on a UV-3600 spectrophotometer. The OPEF measurements were performed by using an HITACHI F-7000 fluorescence spectrophotometer. The concentration of sample solution was 1.0×10^{-5} mol/L. The fluorescence quantum yields (Φ) were determined by using coumarin 307 as the reference according to the literature method [4]. Quantum yields were corrected as follows:

$$\Phi_s = \Phi_r\left(\frac{A_r\eta_s^2 D_s}{A_s\eta_r^2 D_r}\right)$$

Where the *s* and *r* indices designate the sample and reference samples, respectively, *A* is the absorbance at λ_{exc}, η is the average refractive index of the appropriate solution, and *D* is the integrated area under the corrected emission

spectrum[5]. For time-resolved fluorescence measurements, the fluorescence signals were collimated and focused onto the entrance slit of a monochromator with the output plane equipped with a photomultiplier tube (HORIBA HuoroMax-4P) and a time-correlated single-photon counting (TCSPC) card. The decays were analyzed by 'least-squares'. The quality of the exponential fits was evaluated by the goodness of fit (χ^2). The pulse width of the light source: pulse width minimum can be up to 30 ps.

Two-Photon Excited Fluorescence (2PEF) Spectroscopy and Two-Photon Absorption (TPA) Cross-Section

TPA cross-sections (δ) of the samples were obtained by the two-photon excited fluorescence (2PEF) method with a femtosecond laser pulse and a Ti:sapphire system (700-920 nm, 80 MHz, 140 fs) as the light source, data collector was Ocean Optics-USB4000. The concentration of sample solution was 1.0×10^{-4} M. Thus, the δ values of samples were determined by the following Equation (1). $\delta_s=\delta_r\cdot F_s\cdot\Phi_r\cdot C_r\cdot n_r/F_r\cdot\Phi_s\cdot C_s\cdot n_s$ where the subscripts "s" and "r" represent sample and reference (here, fluorescein in ethanol solution at a concentration of 1.0×10^{-4} mol/L was used as reference), respectively. F is the overall fluorescence collection efficiency intensity of the fluorescence signal collected by the fiber spectra meter. Φ, *n* and *c* are the quantum yield of the fluorescence, the refractive index of solvent, and the concentration of the solution, respectively.

As shown in Figures 3 , there is no linear absorption in the wavelength range 600-900 nm for all 6P, which indicates that there are no energy levels corresponding to an electron transition in this spectral range. If frequency upconverted fluorescence appears upon excitation with a tunable laser in this range, it should be safely attributed to multiphoton absorption excited fluorescence. The details of determination conditions are given in the Experimental Section. Detailed experiments revealed that the peak positions of the 2PEF spectra of 6P are independent of the excitation wavelengths, but the emission intensities of the 2PEF are dependent on the excitation wavelengths. The electrons can be pumped to the different excited states by TPA due to the different selection rules, but they would finally relax to the same lowest excited state via internal conversion and/or vibrational relaxation[6].

Otherwise, the molecular 2PA cross-section (δ) determined by Z-scan method can be determined by the following relationship:

$$\delta_s = \frac{\delta_r \times F_s \times \phi_r \times C_r \times n_r}{F_r \times \phi_s \times C_s \times n_s} \qquad (3)$$

Here, the subscripts ref. stands for the reference molecule. δ is the 2PA cross-section value, c is the concentration of solution, n is the refractive index of the solution, F is the 2PEF integral intensities of the solution emitted at the exciting wavelength, and ϕ is the fluorescence quantum yield. The δ_{ref} value of reference was taken from the literature[7]

Third-order nonlinear optical properties (Two-Photon Absorption (2PA))

The third-order NLO properties were measured with concentration of 1.0×10^{-4} mol L^{-1} in DMSO-H_2O solution using the Z-scan technique. For the experiments, the pulse length was 140 fs and the repetition rate was kept at 10 Hz. The filled squares represent the experimental data and the solid line is the theoretical data fitted by using the following equations: [8,9]

$$T(z, s=1) = \sum_{m=0}^{\infty} \frac{[-q_0(z)]^m}{(m+1)^{3/2}} \qquad \text{for } |q_0| < 1$$

$$q_0(z) = \frac{\beta I_0 L_{eff}}{1+x^2}$$

where x = z/z0, z is the distance of the sample and beam focus, $z_0 = \pi\omega_0 2/\lambda$ is the diffraction length of the beam with ω_0 the spotsize at focus, λ is the wavelength of the beam, β was the 2PA coefficient, I0 is the input intensity at the focus (z = 0) calculated by the input energy divided by $\pi\omega_0 2$, Leff = $(1\text{-}e^{-\alpha L})/\alpha$ is the effective length with α the linear absorption coefficient and L the sample length. Furthermore, the molecular 2PA cross-section (σ) could be determined by using the following relationship: [9]

$$\sigma = h\gamma\beta / N_A d \times 10^{-3}$$

here h is the Planck's constant, γ is the frequency of input intensity, NA is the Avogadro constant, and d is the concentration of the sample.

Cell Image

HepG2 cells were seeded in 24 well plates at a density of 2×10^5 cells per well and grown for 96 hours. For live cell imaging cell cultures were incubated with 6P and 10P (10% PBS: 90% cell media) at concentrations 20 μM and maintained at 37°C in an atmosphere of 5% CO_2 and 95% air for incubation times ranging for 30 min. The cells were then washed with PBS. The cells were imaged using confocal laser scanning microscopy and oil immersion lenses. The commercial dyes Mito tracker® was used in the co-localization system, the guidelines for use were download from Life Technologies (www.lifetechnologies.com)

Microscopy

HepG2 cells were imaged on a Zeiss LSM 710 META upright confocal laser scanning microscope using magnification 63× and 100× oil-dipping lenses for monolayer cultures. Image data acquisition and processing was performed using Zeiss LSM Image Browser, Zeiss LSM Image Expert and Image J.

Cytotoxicity Assays in Cells

To ascertain the cytotoxic effect of 6P and 10P treatment over a 24 h period, the 5-dimethylthiazol-2-yl-2,5-diphenyltetrazolium bromide (MTT) assay was performed. HepG2 cells were trypsinized and plated to ~80% confluence in 96-well plates 24 h before treatment. Prior to the compounds' treatment, the DMEM was removed and replaced with fresh DMEM, and aliquots of the compound stock solutions were added to obtain final concentrations of 20, 40, 60, 80 and 100 μM. The treated cells were incubated for 24 h at 37 °C and under 5% CO_2. Subsequently, the cells were treated with 5 mg/mL MTT (40 μL/well) and incubated for an additional 4 h (37 °C, 5% CO_2). Then, DMEM was removed, the formazan crystals were dissolved in DMSO (100 μL/well), and the absorbance at 490 nm was recorded. The cell viability (%) was calculated according to the following equation: cell viability % = OD_{490}(sample)/OD_{490}(control) ×100, where OD_{490}(sample) represents the optical density of the wells treated with various concentration of the compounds and OD_{490}(control) represents that of the wells treated with DMEM + 10% FCS. Three independent trials were conducted, and the averages and standard deviations are reported. The reported

percent cell survival values are relative to untreated control cells.

Two-Photon microscopy in Zebrafish

All procedures involving animals were approved by and conformed to the guidelines of the Southwest University Animal Care Committee, College of Pharmaceutical Sciences. We have taken great efforts to reduce the number of animal used in these studies and also taken effort to reduce animal suffering from pain and discomfort.

Zebrafish larvae after fertilization were incubated at 28 ^{o}C in pure water from Milli-Q system. The 4-day-old zebrafish larvae were fed with 10 μM compounds (**6P** and **10P**) solution at 28 ^{o}C for 5 h, then the larvae were washed with PBS for three times to remove the remaining compounds. Imaging data acquisition and processing were performed using Zeiss LSM Image Browser, Zeiss LSM Image Expert and Image J.

2-imidazolyl-4-methyl-pyrimidine (M)

CuI (0.19 g, 1 mmol), 1,10-phenanthroline (0.6 g, 3 mmol) and DMF (5 mL) were added to a three-necked flask equipped with a magnetic stirrer and a reflux condenser. The reaction mixture turned brown and was kept stirring for 5 min at room temperature, then *t*-BuOK (1.12 g, 10 mmol), pyrazole (0.68 g, 10 mmol), 2-iodide-4-bis-methyl-pyrimidine (0.46 g, 2 mmol), and a catalytic amount of 18-crown-6 were added orderly. After complete addition, the mixture was heated at reflux under nitrogen for about 2h, and cooled to room temperature. The residue was diluted with 200 mL of dichloromethane, washed four times with distilled water, and dried with anhydrous $MgSO_4$. Then it was filtered and concentrated, purified by flash column chromatography on silica. Elution with petroleum/ethyl acetate (6:1 v/v) gave red solid M 0.39 g, Yield: 85%.^{1}H-NMR: (400 MHz, CD_3COCD_3), δ (ppm): 8.523 (s, 1H), 7.185 (s,1H), 7.920 (s, 1H), 7.088 (s, 1H), 2.515 (s, 6H)。 M^+ (MS/ESI), 175.20.

Synthesis of R_1

The compound R_1 was synthesized according to reported methods.[10]

Synthesis of R_2

4-[N, N'-bis(4-ethoxyphenyl)amino]benzaldehyde was prepared referring the literature.[11] Yellow oil was obtained. Yield : 40.7 %. ^{1}H NMR: ((400 Hz, $CD_3)_2CO$), δ (ppm): 9.76(s, 1H) , 7.67 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.8 Hz, 4H), 6.98 (d, J = 8.4 Hz, 4H), 6.78 (d, J = 8.8 Hz, 2H), 4.07 (q, J = 6.9 Hz, 4H), 1.38 (t, J = 7.0 Hz, 6H). IR (KBr, cm^{-1}): 3039, 2974, 2927, 2870, 1690, 1592, 1561, 1505, 1471, 1240, 1161, 826, 717, 684. IE-MS Calcd for $C_{23}H_{23}NO_3$, 361.17; Found, 361.1653.

Synthesis of EX-6

0.67 g (6 mmol) t-BuOK was placed into a dry mortar and well milled into powder with heating, then 2-(1H-imidazol-1-yl)-4,6-dimethylpyrimidine (0.17 g, 1 mmol) and R1 (1.30 g, 4 mmol) were added and milled vigorously for about 5 min. The sticky crude product was obtained. The mixture was dissolved with CH_2Cl_2 and extracted with water (*ca*. 3×100 mL). Then it was dried with anhydrous $MgSO_4$, filtered, concentrated. The crude product was purified by chromatography on a silica gel with ethyl acetate /ethanol mixture as the eluent. The red sticky product (0.51g) was collected. Yield：65%. IR (KBr, cm^{-1}) selected bands: 3425 (w), 3074 (m), 3037 (s), 2922 (s), 2622 (w), 1602 (s), 1568 (s), 1519 (s), 1468 (s), 1424 (s), 1376 (s), 1322 (s), 1235 (s), 1183 (s), 1109 (s), 1023 (s), 978 (s), 889

(s), 836 (s), 810 (s), 750 (m), 724 (w), 685 (m), 655 (m), 565 (w), 521 (s). ^{1}H-NMR: (400 MHz, CD_3COCD_3), δ (ppm): 3.31 (s, 12H), 3.52 (d, J = 4 Hz, 8H), 3.61 (d, J = 4 Hz, 8H), 3.69 (s, 16H), 6.85 (d, J = 8 Hz, 4H), 7.00 (d, J = 16 Hz, 2H), 7.27 (s, 1H), 7.59 (d, J = 8 Hz, 4H), 8.06 (d, J = 16 Hz, 2H), 7.12 (s, 1H), 8.11 (s, 1H), 8.73 (s, 1H). ^{13}C-NMR (CD_3COCD_3, 100MHz), δ (ppm): 51.76, 58.95, 69.28, 71.24, 72.73, 112.61, 114.14, 117.65, 120.7, 124.2, 130.5, 130.8, 136.89, 139.1, 150.3, 155.3, 166.0. MS: $C_{43}H_{60}N_6O_8$, 788.97, Found: 789.45 ([M+H]$^+$, 46), 811.43 ([M+Na]$^+$, 75)；MALDI-TOF, m/z (%): 789.29 ([M+H]$^+$,100). Anal. Calcd. For $C_{43}H_{60}N_6O_8$:C,65.46;H,7.67;N,10.65;Found: C,65.41; H, 7.67;N,10.66.

Synthesis of EX-10

t-BuOK (0.56 g, 5 mmol), R_2 (0.80 g, 2.2 mmol) and 2-(1H-imidazol-1-yl)-4,6-dimethylpyrimidine (0.17 g, 1 mmol) were mixed together, and milled vigorously for about 10 min. The reaction was monitored by TLC (petroleum/ethyl acetate 4:1 v/v). After the reaction was completed, the mixture was dispersed in 200 mL distilled water. The solution was extracted with CH_2Cl_2 several times. The organic layer was washed with water, saturated brine and dried over anhydrous $MgSO_4$. After removing solvent under reduced pressure, the residue was purified by flash chromatography on silica gel using petroleum/ethyl acetate (8:1 v/v) as eluent 0.25 g, yield: 55%. FT-IR (KBr, cm^{-1}) selected bands: 3407 (s), 2926 (s), 1576 (s), 1511 (s), 1479 (s), 1391 (s), 1326 (s), 1222 (s), 1142 (s), 1038 (s), 660 (s). ^{1}H-NMR: (400 MHz, CD_3COCD_3), δ (ppm): 1.40-1.44 (t, J=8.00, 12H), 4.00-4.05 (m, 8H), 6.80-6.91 (m, 12H), 6.91-6.95 (d, J=16.00, 2H), 7.07- 7.10 (d, J=12.00, 7H), 7.15-7.17 (d, J=8.00, 2H), 7.39-7.41 (d, J=8.00, 4H), 7.83-7.87 (d, J=16.00, 2H), 7.90 (s, 1H), 7.97 (s,2H).^{13}C-NMR (100MHz, CD_3COCD_3): 165.09, 156.30, 150.42, 139.68, 137.76, 135.98, 129.97, 129.86, 129.00, 127.54, 126.96, 121.69, 121.69, 116.57, 115.46, 63.40, 14.24. MALDI-TOF, m/z (%)：860.18 ([M+H]$^+$, 100). Anal. Calc. for $C_{55}H_{52}N_6O_4$: C, 76.72; H, 6.07; N, 9.73, O, 7.43. Found: C, 76.48; H, 5.81; N, 13.84, O, 7.42.

Synthesis of 6

Using a 50-mLthree-neck flask fitted with a stirrer, thermometer, and condenser, 0.79 g (1 mmol) of EX-6 and 0.17 g (1.1 mmol) of methyl iodide were mixed in toluene. The solution was stirred at room temperature for **2** h and then refluxed for 30 min. After cooling, the solution was filtered and the solid was washed with ethyl ether. The yellow solid (0.78g, 0.84 mmol) was dried. yield: 55%.

Synthesis of 10

10 was prepared by a procedure similar to that of 6 but with EX-10 (0.43 g, 0.5 mmol), yield: 96%.

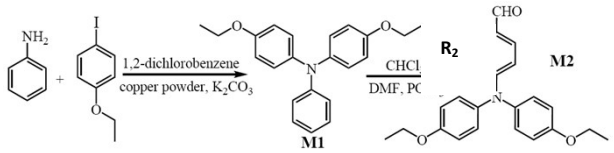
Synthesis of 6P

Using a 50-mL oneneck flask fitted with a stirrer and a condenser, 0.93 g (1.0 mmol) 6**,** 0.28 g (1.1 mol) $AgPF_6$**,** and 30 mL of absolute acetonitrile were mixed. Then the solution was heated to reflux overnight. A red solid was filtered after cooling. After removing solvent under reduced pressure, the deep yellow solid (0.83g, 0.88mmol) was washed with acetonitrile and water each two times, yield: 88%.FT-IR (KBr, cm^{-1}) selected bands: 840.97 (s) ($^-PF_6$). ^{1}H-NMR: (400 MHz, $CDCl_3$), δ(ppm): 3.36~3.39 (t, J=6.00 Hz, 12H), 3.55~3.56 (d, J=4.00 Hz, 16H), 3.62~3.66 (t, J=8.00 Hz, 16H), 3.94 (s, 3H), 6.60~6.64 (d, J=15.60 Hz, 2H), 6.68~6.70 (d, J=8.00 Hz, 4H), 7.24 (s, 1H), 7.63~7.65 (d, J=8.00

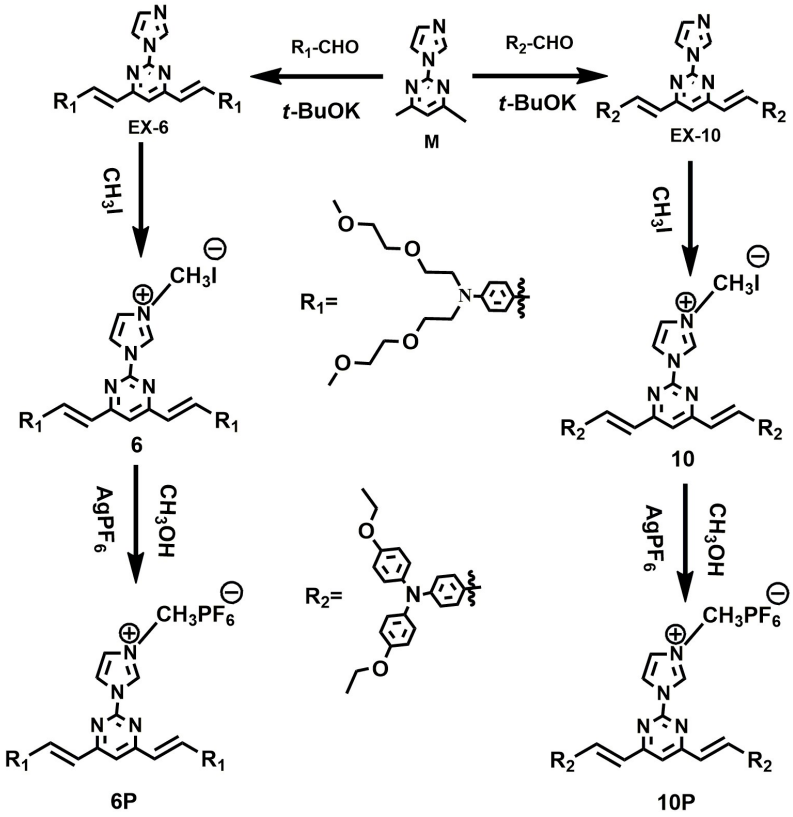
Hz, 1H), 7.70~7.72 (d, *J*=8.00 Hz, 1H), 7.47~7.49 (d, *J*=8.00 Hz, 4H), 7.82~7.86 (d, *J*=16.00 Hz, 2H), 8.26 (s,1H). ^{13}C-NMR($CDCl_3$, 100 MHz), δ (ppm): 40.59, 50.94, 59.12, 68.37, 71.97, 111.49, 114.97, 115.16, 115.36, 124.01, 124.63, 130.22, 133.06, 143.52, 149.40, 155.98, 156.62, 165.07. MALDI-TOF, m/z(%): 803.79([M-PF_6] ,100).

Synthesis of 10P

10P was prepared by a procedure similar to that of 6P but with 10 (1.0 g, 1 mmol), yield: 85%. FT-IR (KBr, cm^{-1}) selected bands: 843.17 (s) ($^-$PF6). ^{1}H-NMR (400 MHz, d_6-DMSO, ppm): δ 1.23 (s, 3 H), 1.31~ 1.35 (q, 12 H, J=10.0 Hz), 2.33 (s, 1 H), 4.00~ 4.05 (q, 8 H, J=14.0 Hz), 6.34 (d, 4 H, J=4.0 Hz), 6.94~ 6.97 (d, 8 H, J=12.0 Hz), 7.06~ 7.13 (m, 12 H, J=20.0 Hz), 7.54 (d, 4 H, J=8.0 Hz), 7.96 (d, 1 H, J=8.0 Hz), 8.06~ 8.10 (q, 2 H, J=8.0 Hz); ^{13}C-NMR (100MHz, CD3COCD3):165.42, 156.51, 150.93, 139.95, 136.38, 130.87, 129.35, 127.73, 124.92, 119.94, 119.16, 117.93, 115.51, 63.40, 36.54, 14.22. MALDI-TOF, m/z(%): 875.49 ([M-PF_6] ,100).



Scheme S1 Synthetic routes for R_2



Scheme S2 Synthetic routes for 6P and 10P

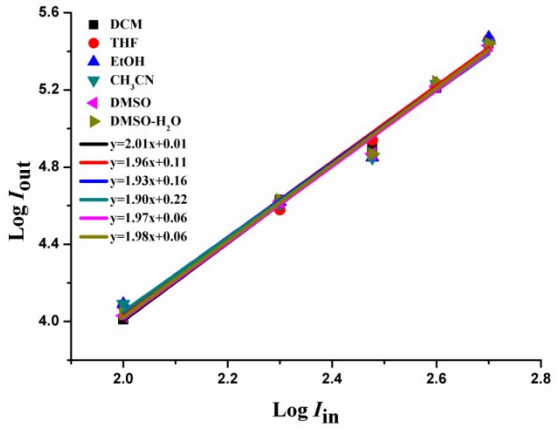


Fig. S1 Output fluorescence intensity (I_{out}) vs. the square of input laser power $(I_{in})^2$ for L1 and L2 in benzene. Excitation carried out at 800 nm, with c = 1.0×10^{-4}mol L^{-1} in six organic solvents.

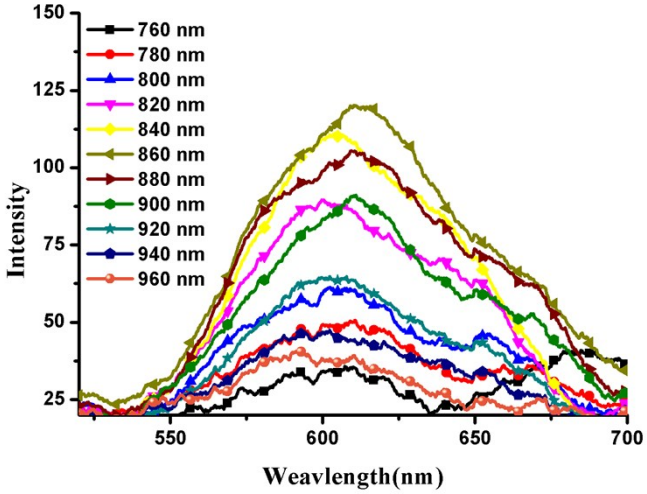


Fig.S2 The two-photon excited fluorescence spectra of 6P in DCM, with c=1×10^{-4}mol L^{-1}.

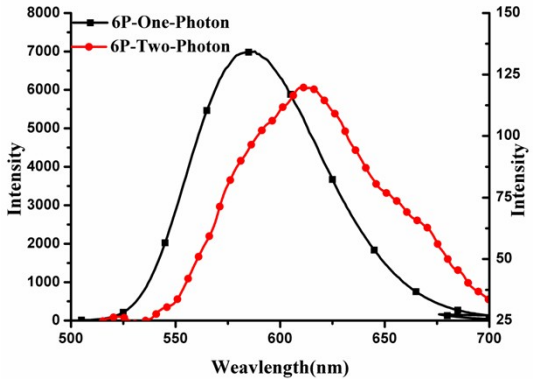


Fig. S3 (a) The single-photon(c=1×10^{-4}mol L-1) and two-photon excited fluorescence spectra(c=1×10^{-4} mol L-1) of 6P in DCM.

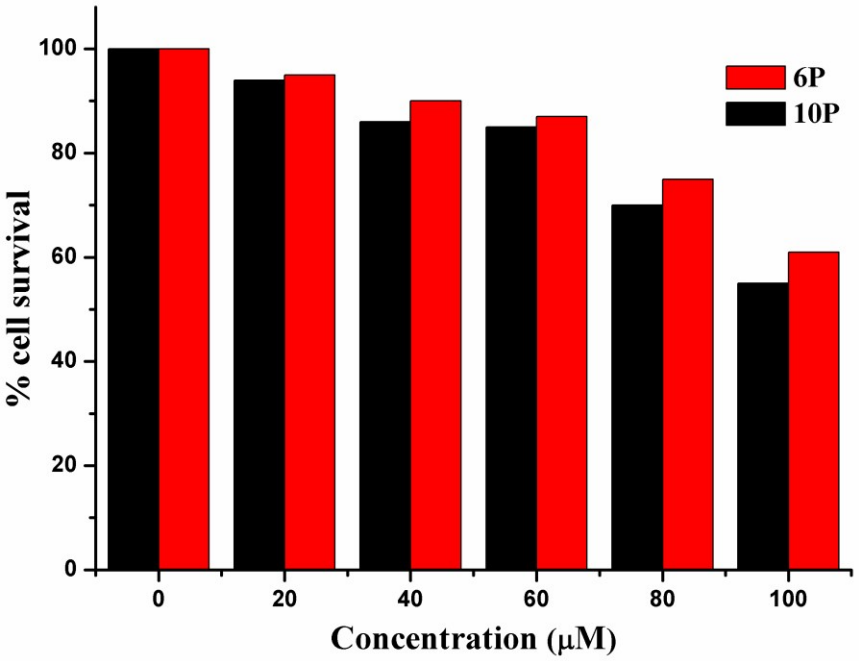


Fig. S4. Cytotoxicity data results obtained from the MTT assay.

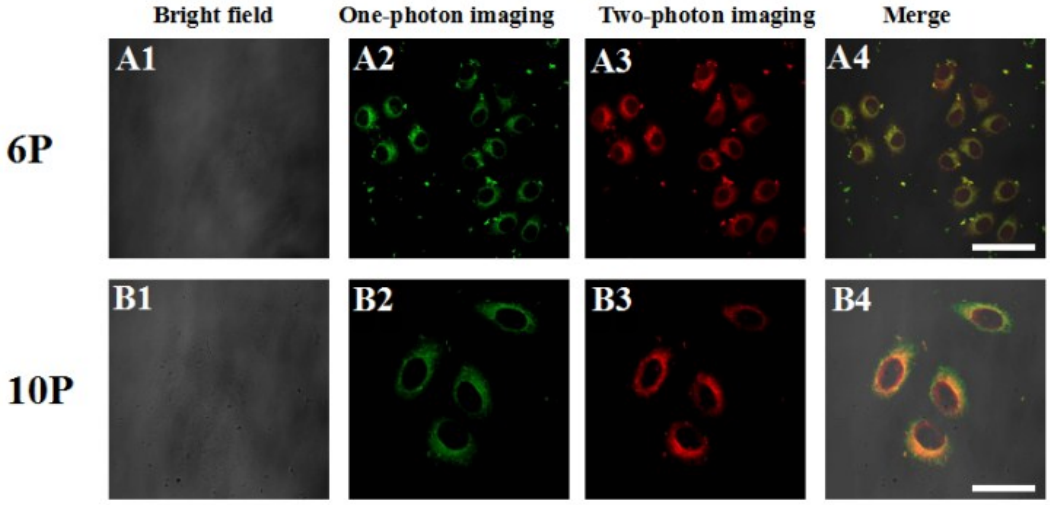


Figure S5 (A1) Bright field image of HepG2 cells incubated with 10 μM 6P after 30 min of incubation, washed by PBS buffer. (A2) One-photon image of HepG2 cells incubated with 10 μM 6P after 30 min of incubation, washed by PBS buffer. λ_{ex} = 458 nm (emission wavelength from 550 to 600 nm). (A3) Two-photon image of HepG2 cells incubated with 10 μM 6P after 30 min of incubation, washed by PBS buffer. λ_{ex} = 830 nm (emission wavelength from 550 to 650 nm). (A4) The overlay of (A1) to (A3). (B1) Bright field image of HepG2 cells incubated with 10 μM10P after 30 min of incubation, washed by PBS buffer. (B2) One-photon image of HepG2 cells incubated with 10 μM 10P after 30 min of incubation, washed by PBS buffer. λ_{ex} = 405 nm (emission wavelength from 550 to 600 nm). (B3) Two-photon image of HepG2 cells incubated with 10 μM 10P after 30 min of incubation, washed by PBS buffer. λ_{ex} = 840 nm (emission wavelength from 600 to 650 nm). (B4) The overlay of (B1) to (B3).

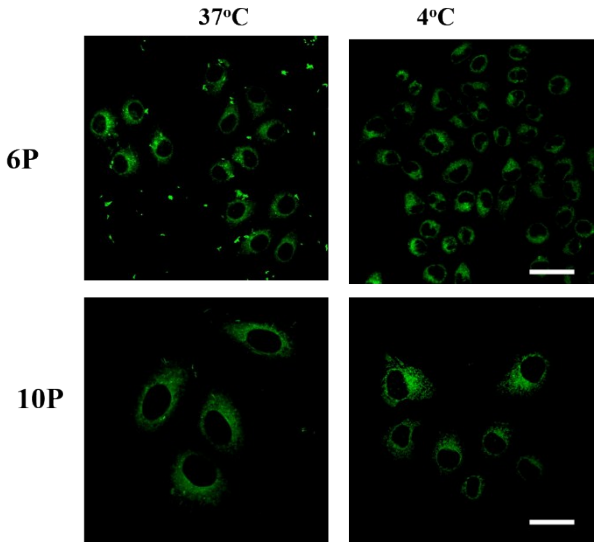


Fig S6. Two-photon image of HepG2 cells incubated with **6P** and **10P** at 37 °C and 4 °C for 30 min.

Table S1 Ab initio calculation data of linear absorption spectra, the experimental data of linear absorption spectra, and oscillator strengths of 6P and 10P in DMSO

	6P	**10P**
$\lambda_{ab\text{-}OPA}$ (nm) (calculated) [a]	486.58	390.61
$\lambda_{ab\text{-}OPA}$ (nm) (experiment, DMF)	483.00	372.00
f [b]	0.52	0.28
OI and Tc[c]	218 (H-1)→221 (L+1) (0.63) 219 (H)→221 (L+1) (0.14)	266(H-1)→270(L+2) (0.60) 265(H-1)→269(L+1) (0.20)

[a] The TD-DFT calculation data of one-photon absorption spectra with the peak position of the maximum absorption band (nm), [b] Oscillator Strengths (f) [c] The excited states computed by TDDFT Method with the Orbitals Involved (OI) in the Excitations Including Transition Coefficients (Tc)

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