Constructing Ultralong Near-infrared Organic Phosphorescence Materials with 732 nm through One-axis Two-wing Guest-Host Strategy for Bioimaging

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1. Materials, Characterization and Molecular dynamics (MD) simulations.

1H and 13C NMR spectra were carried out by a Bruker ARX500 spectrometer with CDCl3 as the solvent. UV-vis absorption spectra were measured by a Persee TU-1901 spectroscopy. Fluorescence spectra were measured by a Hitachi F-7000 spectrophotometer. Phosphorescence spectra were measured by a FLS920 lifetime and steady state spectrometer. X-Ray crystal structure analyses were conducted on a Bruker-AXS SMART APEX2 CCD diffractometer. Solid-state emission quantum yields (Φ) were collected on a FluoroMax-4 (Horiba Jobin Yvon) fluorimeter equipped with integrated sphere. Solid-state emission quantum yields (Φ) were collected by using FluoroMax-4 (Horiba Jobin Yvon) fluorimeter equipped with integrated sphere. The emission decay data were analyzed using DAS-6 Fluorescence Decay Analysis software with 2 exponential analysis the program. The quality of the exponential fits was evaluated by the χ2 of <2.0. The atom types and parameters of Py and BPO were built from the general AMBER force field. To obtain the partial charge of each atom of two molecules, the electrostatic potential of two molecules were calculated at the B3LYP/6-31G* level based on the optimized geometric structures using Gaussian 16 package1. The partial charges of the atoms reproducing the electrostatic potential of two molecules were obtained by using restrained electrostatic potential (RESP)2, 3 fit method. In order to simulate Py/BPO system, we firstly built a 4.6×3.1×4.4 nm TPA unit cell with 192 TPA molecules, and then a Py molecule was placed in the position vacated by the one host molecules to obtain the Py/BPO model as an initial model. For MD simulations, firstly, the energy minimization was performed by using steepest descent algorithm and the conjugate gradient, then we performed the 500 ps MD simulations under the NVT (P = 1 bar, T = 10 K) ensemble. The temperature was controlled by the velocity rescaling thermostat4.
Then we performed the 10 ns MD simulations under the NPT (P = 1 bar, T = 10 K) ensemble coupled by Parrinello-Rahman barostat scheme. The Newton's classical equations of motion were integrated at a time step of 2 fs using the classical leapfrog algorithm. Trajectory analysis was done with the help of utility tools included in the GROMACS (version 5.1.5) and VMD packages.

2. Molecular structure of organic RTP materials
Scheme 1. Organic RTP materials that have been reported.

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3. Synthesis of target compounds

The Pyrene compound is directly purchased commercially and purified by column chromatography twice. Pyrene (Py) $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 8.29 (d, $J = 7.6$ Hz, 4H), 8.19 (s, 4H), 8.07 (d, $J = 7.6$ Hz, 2H), ppm. $^{13}$C NMR (125 MHz, DMSO-$d_6$) $\delta$: 130.7, 127.3, 126.2, 125.1, 123.9 ppm. HRMS (ESI) m/z: [M+H]$^+$ calculated for C$_{16}$H$_{11}$, 203.0863; found, 203.0855.

Synthesis of pyrene derivatives.

The mixture of compound 1 or compound 2 (10.0 mmol), boronic acid (12.0 or 24.0 Pd(PPh$_3$)$_4$ (5.0 mol%), and K$_2$CO$_3$ (5.0 mol%) were dissolved in THF (10.0 mL) and water (1.0 mL). The mixture was stirred for 12 h at 80°C under nitrogen atmosphere. The solvent was removed under reduced pressure, and the residue were purified by column chromatography (petroleum ether: ethyl acetate = 1:100, v : v) to afford the pure MOPy/MAPy/DMOPy/DMAPy compounds.
1-(4-Methoxyphenyl)pyrene (MOPy): White solid (2.22g, 72%). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 8.34-8.08 (m, 8H), 7.98 (d, $J = 7.6$ Hz, 1H), 7.55 (d, $J = 8.4$ Hz, 2H), 7.16 (d, $J = 8.4$Hz, 2H), 3.87 (s, 3H) ppm. $^{13}$C NMR (125 MHz, DMSO-$d_6$) $\delta$: 158.8, 137.0, 132.5, 131.5, 131.1, 130.5, 129.9, 127.8, 127.6, 127.5, 127.3, 126.4, 125.3, 125.0, 124.9, 124.8, 124.3, 124.2, 114.2 ppm. HRMS (ESI) m/z: [M+H]$^+$ calculated for C$_{23}$H$_{17}$O, 309.1274; found, 309.1278.

N,N-dimethyl-4-(pyren-1-yl)aniline (MAPy): Green solid (2.09g, 65%). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 8.31-8.04 (m, 8H), 7.97 (d, $J = 7.6$ Hz, 1H), 7.46 (d, $J = 8.4$ Hz, 2H), 6.93 (d, $J = 8.4$ Hz, 2H), 3.00 (s, 6H) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 149.7, 137.8, 131.1, 131.0, 130.6, 129.5, 127.8, 127.7, 127.65, 127.5, 127.2, 127.0, 126.3, 125.1, 125.0, 124.7, 124.4, 124.3, 112.4 ppm. HRMS (ESI) m/z: [M+H]$^+$ calculated for C$_{24}$H$_{19}$N, 322.1590; found, 322.1583.

1,6-Bis(4-methoxyphenyl)pyrene (DMOPy): Green solid (2.28g, 55%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.19 (t, $J = 8.0$ Hz, 4H), 8.03 (d, $J = 9.2$ Hz, 2H), 7.97 (d, $J = 8.0$ Hz, 2H), 7.58 (d, $J = 8.4$ Hz, 4H), 7.12 (d, $J = 8.4$ Hz, 4H), 3.94 (s, 6H) ppm. HRMS (ESI) m/z: [M+H]$^+$ calculated for C$_{30}$H$_{23}$O$_2$, 415.1693; found, 415.1691.

4,4’-(pyrene-1,6-diyl)bis(N,N-dimethylaniline) (DMAPy): Green solid (2.33g, 53%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 8.26 (d, $J = 9.0$ Hz, 2H), 8.15 (d, $J = 8.0$ Hz, 2H), 7.99 (q, $J = 9.0$ Hz, 4H), 7.55 (d, $J = 8.5$ Hz, 4H), 6.94 (d, $J = 8.5$ Hz, 4H), 3.08 (s, 12H) ppm. HRMS (ESI) m/z: [M+H]$^+$ calculated for C$_{32}$H$_{29}$N$_2$, 441.2325; found, 441.2334.

4. Experimental data

(a) (b) (c) (d) (e)
Fig. S1. High performance liquid chromatography of Py (a), MOPy (b), MAPy (c), DMOPy (d), DMAPy (e) (CH$_3$OH/H$_2$O= 80%: 20%)
Fig. S5. Fluorescence spectra of guest-host materials. (Ex.: 360 nm)

Fig. S6. CIE coordinates of delayed emission of guest-host materials.

Fig. S7. Fluorescence decay curves of guest-host materials. (Ex.: 360 nm)
**Fig. S8.** Absorption spectra of guest-host materials.

**Fig. S9.** The phosphorescence spectra of the guests in 77 K (Delayed time: 5 ms; Ex: 380 nm; Concentration: $1 \times 10^{-5}$ mol/L; Solvent: 2-methyltetrahydrofuran).

**Fig. S10.** (a) The molecular configuration of BPO in single crystal. (b) The molecular configuration of BPO in simulated Py/BPO system.
Fig. S11. Molecular packing along the a-axis (a), b-axis(b), c-axis(c) of BPO single crystal.

Fig. S12. Molecular packing along the a-axis (a), b-axis(b), c-axis(c) of simulated Py/BPO guest-host system.
4. Bio-imaging measurement

Materials.
The amphiphilic co-polymer PEG-b-PPG-b-PEG (F127) was purchased from Aladdin Ltd. Fetal bovine serum (FBS) was provided by Thermo Fisher Scientific Inc. (Waltham, MA, USA). Transmission electron microscopy (TEM) images were acquired from a JEM-2010F transmission electron microscope with an accelerating voltage of 200 kV. Dynamic light scattering (DLS) was measured on a 90 plus particle size analyzer. In vitro and in vivo phosphorescence imaging was performed by IVIS® Lumina II imaging system.

Preparation of nanoparticles.
To 1 mL of the aqueous solution of F127 (10 mg), the DMAPy/BPO crystals (1 mg) were added. The mixture was then sonicated by a microtip-equipped probe sonicator (Branson, S-250D) for 10 min. The resultant suspension was filtered through a 0.45 μm syringe driven filter to afford solution of nanoparticles. And then the resultant solution was concentrated.

In vitro phosphorescent imaging of nanoparticles solutions.
The phosphorescent intensities of DMAPy/BPO and DOB/BPO nanoparticles were recorded using IVIS® Lumina II imaging system at t = 10 s after each kind of nano solutions were irradiated by 365 nm handheld UV lamp (12 W) for 1 min. The IVIS
system was set in bioluminescence mode with open/GFP/Dsred filter setting (exposure time: 17 s).

**Cell Culture.**

4T1 breast cancer cells were obtained from American Type Culture Collection (ATCC). The cells were cultured in DMEM (Dulbecco’s Modified Eagle Medium) (GIBCO) supplemented with 10% FBS and 1% penicillin streptomycin at 37 °C in a humidified environment containing 5% CO₂, which were regularly checked for mycoplasma contamination.

**Cytotoxicity Study.**

*In vitro* cytotoxicities of the nanocrystals against cancer cells were assessed by 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide (MTT) assay. Briefly, 4T1 breast cancer cells seeded in 96-well plates (Costar, IL, USA) were exposed to each kind of nanocrystals at the RTP dye concentrations of 25, 50, 100, 200, 400 μg mL⁻¹, respectively, at 37 °C. After 8 h incubation, the wells were washed twice with 1×PBS, and 100 μL of freshly prepared MTT (0.5 mg mL⁻¹) solution in culture medium was added into each well. The MTT medium solution was carefully removed after 3 h incubation in the incubator. DMSO (100 μL) was then added into each well and the plate was gently shaken for 10 min at room temperature to dissolve all the precipitates formed. The absorbance of MTT at 490 nm was monitored by the microplate reader (Genios Tecan). Cell viability was expressed by the ratio of absorbance of the cells incubated with nanoparticles suspension to that of the cells incubated with culture medium only.

**Animals and tumor models.**

Six-weeks-old BALB/c nude mice were purchased from the Laboratory Animal Center of the Academy of Military Medical Sciences (Beijing, China).

To establish the armpit tumor-bearing mouse model, 5 × 10⁵ 4T1 cancer cells in 100 μL of cell culture medium were injected into the armpit of healthy mice. After about 7 days, the armpit tumor was formed.

**Statement of ethical approval**

All animal studies were performed according to the guidelines set by the Tianjin Committee of Use and Care of Laboratory Animals, and the overall project protocols were approved by the Animal Ethics Committee of Nankai University. The accreditation number of the laboratory is SYXX(Jin) 2019-0003 promulgated by Tianjin Science and Technology Commission.

**In vivo imaging.**

**Subcutaneous phosphorescent imaging with nanoparticles.** The healthy nude mice were anesthetized using 2% isoflurane in oxygen and placed into the box of IVIS® instrument. Then, 100 μL of the DMAPy/BPO and DOB/BPO nanoparticles were subcutaneously injected into the mice, respectively, followed by irradiating by 365 nm hand-held UV lamp (12 W) for 1 min and imaging with IVIS® instrument. During the imaging process, the mice were warmed with a heating pad under continued isoflurane anesthesia. The phosphorescent images were acquired in bioluminescence mode with open filter setting (exposure time: 17 s) and in fluorescence mode with Dsred filter setting (excitation: 430 nm, exposure time: auto).
Phosphorescent imaging of sentinel lymph node. The healthy nude mice were anesthetized using 2% isoflurane in oxygen and placed into the box of IVIS® instrument. Then, 100 μL of the DMAPy/BPO nanoparticles were into the forepaws of live nude mice, followed by irradiating with 365 nm hand-held UV lamp (12 W) for 1 min and imaging with IVIS® instrument. During the imaging process, the mice were warmed with a heating pad under continued isoflurane anesthesia. The phosphorescent images were acquired in bioluminescence mode with open filter setting (exposure time: 17 s) and in fluorescence mode with Dsred filter setting (excitation: 430 nm, exposure time: auto).

Phosphorescent imaging of armpit tumor in vivo. 200 μL of DMAPy/BPO nanoparticles (4 mg mL⁻¹ based on nanoparticles) were injected into the armpit tumor-bearing mice via the tail vein. At 6 h post-injection, the tumor bearing mice were irradiated with 365 nm hand-held UV lamp (12 W) for 1 min. During the imaging process, the mice were warmed with a heating pad under continued isoflurane anesthesia. The phosphorescent images were acquired in bioluminescence mode with open filter setting (exposure time: 17 s) and in fluorescence mode with Dsred filter setting (excitation: 430 nm, exposure time: auto). After that, the mice were sacrificed and main tissues including heart, lung, spleen, kidneys and liver were excised. These organs were imaged with the same conditions in fluorescence mode to obtain the phosphorescence signals.

Statistical analysis
Quantitative data were expressed as mean ± standard deviation (SD). Statistical comparisons were made by ANOVA analysis and two-sample Student’s t-test. p value < 0.05 was considered statistically significant.

Fig. S15. Diameter distribution of DOB/BPO nanoparticles. Inset: TEM image, scale bar = 100 nm.
**Fig. S16.** The phosphorescence intensities for DMAPy/BPO nanoparticles with varying UV exposure time. Error bars, mean ± standard deviation (n = 3).

**Fig. S17.** (a) The phosphorescence intensities of DOB/BPO nanoparticles as a function of the cycle number of UV light irradiation (n = 3). (b) The phosphorescence intensities for DOB/BPO nanoparticles with varying UV exposure time. Error bars, mean ± standard deviation (n = 3).

**Fig. S18.** The phosphorescence intensities as a function of the concentration of DMAPy/BPO nanoparticles (n = 3).

**Fig. S19.** The phosphorescence signals of different organs (1-heart, 2-liver, 3-spleen, 4-lung and 5-
kidney) from tumor-bearing mice at 6 h post intravenous injection of DMAPy/BPO nanoparticles.

**Fig. S20.** H&E-stained image indicated that the light-up tissue was tumor.

**Fig. S21.** H&E-stained images of major organs of the tumor-bearing mice after intravenous injection of saline and DMAPy/BPO nanoparticles, respectively.
5. NMR spectra

Fig. S22. $^1$H NMR of compound Py (DMSO-$d_6$, 400 MHz).

Fig. S23. $^{13}$C NMR of compound Py (DMSO-$d_6$, 125 MHz).
Fig. S24. $^1$H NMR of compound MOPy (DMSO-$d_6$, 400 MHz).

Fig. S25. $^{13}$C NMR of compound MOPy (DMSO-$d_6$, 125 MHz).
Fig. S26. $^1$H NMR of compound MAPy (DMSO-$d_6$, 400 MHz).

Fig. S27. $^{13}$C NMR of compound MAPy (DMSO-$d_6$, 125 MHz).
**Fig. S28.** $^1$H NMR of compound DMOPy (CDCl$_3$, 400 MHz).

**Fig. S29.** $^1$H NMR of compound DMAPy (CDCl$_3$, 500 MHz).