

Supplementary Information

Diphenyl-1-pyrenylphosphine: Photo-triggered AIE/ACQ transition with remarkable third-order nonlinear optical signal change

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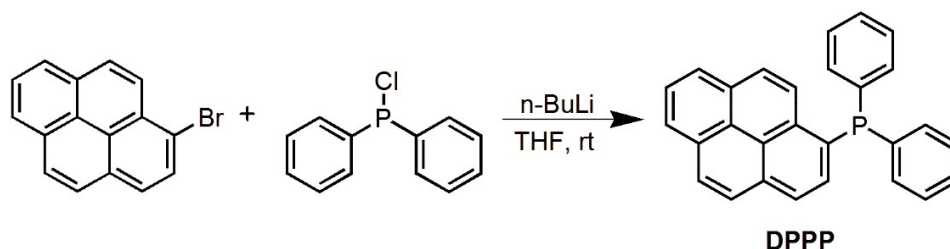
1. Reagents

Unless particularly stated, all raw materials and reagents used in this work are commercially available without further treatment and purification. 1-bromopyrene, chlorodiphenylphosphine, n-butyllithium were ordered from Energy Chemical Co., Shanghai, China. All the other organic solvents were purchased from Sinopharm Chemicals Beijing Co. Beijing, China. Deionized water was used throughout the experiments. 10 mmol·L⁻¹ phosphate buffer solutions (PBS) with pH = 7.0 were prepared using different ratios of phosphoric acid, sodium dihydrogen phosphate and sodium hydroxide. The pH values of the buffer solutions were detected using a pH meter at room temperature.

2. Apparatus

Fluorescence spectra were obtained by using a JASCO FP-8300 spectrometer. Absorption spectra were recorded by using a JASCO-750 UV-vis spectrometer. The crystallographic data were collected on a Bruker ADVANCE with graphite monochromated Mo K α radiation ($\lambda=0.71073\text{\AA}$). Dynamic light scattering (DLS) experiments were measured on a NanoPlus-3 DLS particle size/zeta potential analyzer. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV400 NMR spectrometer. Electrospray Ionization Mass Spectrometry (ESI-MS) were undertaken using a Shimadzu LCMS-IT/TOF high resolution liquid phase-electrospray-ion trap/time of flight series mass spectrometer. The photos were recorded by a Nikon D5500 camera. Nonlinear absorption data were investigated using an NLO-IZ Z-scan meter and integrated optical limiter. A Q-switched Nd: YAG 532 nm laser (GKPPL-1064-1-10, Beijing GK Laser technology Co., Ltd) was used as the light source, which provided linearly polarized 21 ps pulses with a repetition rate of 10 Hz at 532 nm. Unless otherwise noted, all the measurements in this work were performed at room temperature.

3. Synthesis



Scheme S1. Synthetic route of compound **DPPP**.

Diphenyl-1-pyrenylphosphine (DPPP): 1-bromopyrene (3.0 mmol, 0.84 g) was first dissolved in 20 mL THF and rapidly cooled to $-78\text{ }^{\circ}\text{C}$. Then n-butyllithium in hexane (1.0 mL, 2.0 mmol) was added using a syringe and stirred for 1 h. Next, chlorodiphenylphosphane (2.5 mmol, 0.55 g) was added to the organolithium solution, and the mixed solution was allowed to warm up to room temperature. After 18 h, 10 mL water was added slowly, and THF was removed by reduced pressure evaporation. The resulting aqueous phase was extracted with 30 mL dichloromethane. Then the combined organic phase was washed with 20 mL water. The organic phase was then dried over anhydrous sodium sulfate and filtered, and the solvent was removed by reduced pressure evaporation. **DPPP** was obtained as a white solid with a yield of 61%. $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ (ppm): 8.65 (dd, $J = 9.2, 4.8$ Hz, 1H), 8.35 (dd, $J = 14.7, 7.4$ Hz, 2H), 8.29-8.21 (m, 3H), 8.21-8.08 (m, 2H), 7.50 (dd, $J = 7.9, 4.3$ Hz, 1H), 7.45-7.40 (m, 6H), 7.30-7.26 (m, 4H). $^{31}\text{P-NMR}$ (162 MHz, DMSO) δ (ppm): -15.18 (s). HRMS spectrometry: m/z calcd for $[\text{M} + \text{H}]^+$: 387.1297; found: 387.1299. Luminescence quantum yield of **DPPP** was 15.1%.

Diphenyl-1-pyrenephosphinoyl (O-DPPP): **DPPP** was irradiated by UV light in EtOH for 2 h. After removing the solvent under reduced pressure, **O-DPPP** was obtained. $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ (ppm): 8.84 (d, $J = 9.7$ Hz, 1H), 8.44 (d, $J = 7.5$ Hz, 1H), 8.40-8.35 (m, 2H), 8.32 (dd, $J = 8.0, 2.2$ Hz, 1H), 8.25 (dt, $J = 9.4, 4.8$ Hz, 3H), 8.20-8.14 (m, 1H), 7.73 (dt, $J = 11.0, 5.5$ Hz, 1H), 7.70-7.62 (m, 6H), 7.61-7.54 (m, 4H). $^{31}\text{P-NMR}$ (162 MHz, DMSO) δ (ppm): 30.58 (s). HRMS spectrometry: m/z calcd for $[\text{M} + \text{H}]^+$: 403.1246; found: 403.1247. Luminescence quantum yield of **O-DPPP** was 3.3%.

4. Selected spectra and data referred in the paper

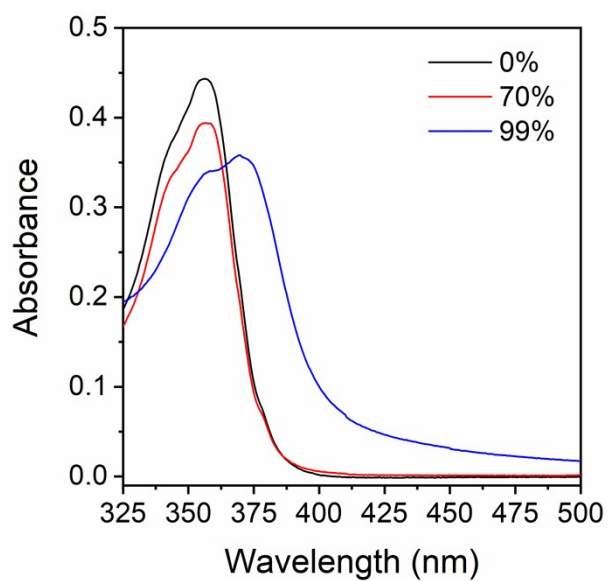


Figure S1. Absorption spectra of **DPPP** in H₂O/EtOH mixtures with f_w of 0%, 70% and 99%. Conditions: the concentrations of **DPPP** were 10 $\mu\text{mol}\cdot\text{L}^{-1}$.

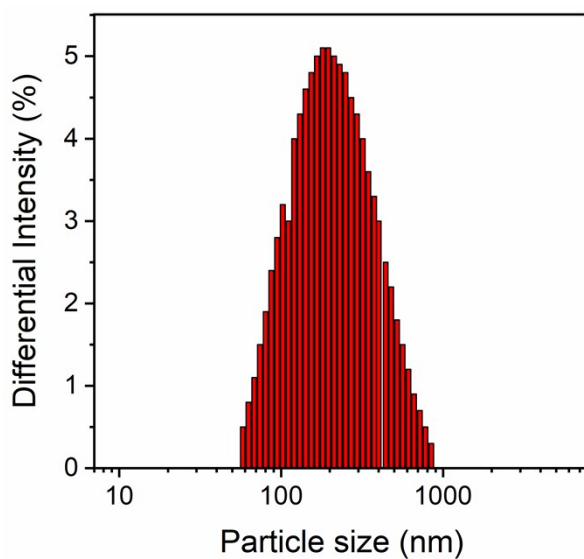


Figure S2. DLS result of **DPPP** in H₂O/EtOH mixtures with f_w of 99%.

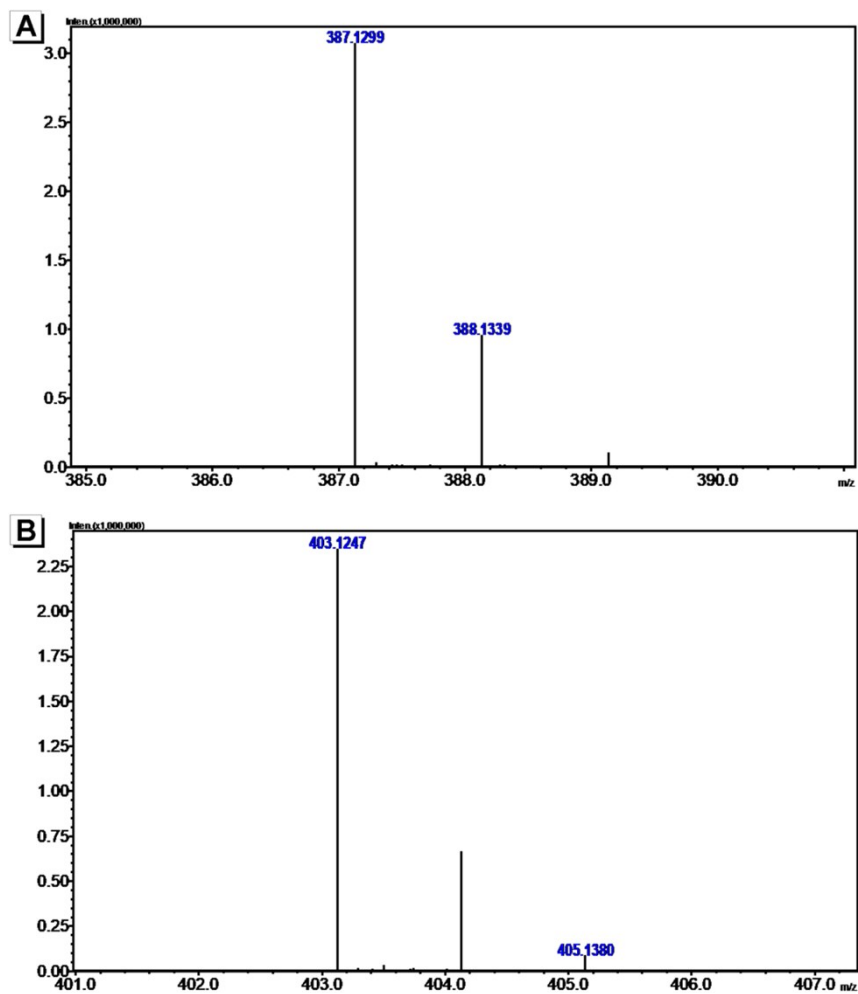


Figure S3. HRMS spectrum of DPPP A) before and B) after UV light irradiation.

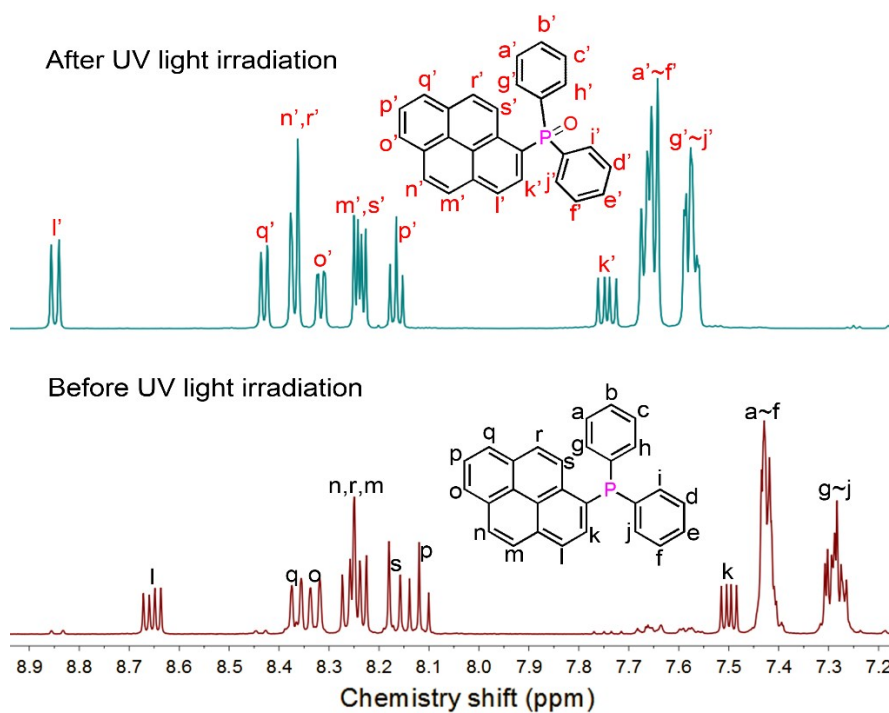


Figure S4. ¹H-NMR spectra of DPPP before and after UV light irradiation.

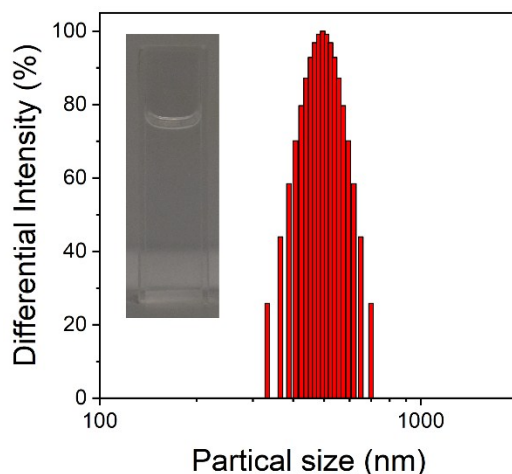


Figure S5. DLS result and photo of **O-DPPP** in H₂O/EtOH mixtures with f_w of 99%.

Table S1. Crystallographic data and structure refinement details for **DPPP** and **O-DPPP**.

Complex	DPPP	O-DPPP
Formula	C ₂₈ H ₁₉ P	C ₂₈ H ₁₉ OP
CCDC	1973777	1973778
F_w	386.40	402.40
Temp.(K)	273.15	293
Wavelength(Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P 2_1/c$	$P 2_1/c$
a(Å)	9.0803(11)	9.042(10)
b(Å)	21.343(3)	21.62(3)
c(Å)	21.376(3)	21.34(3)
α (°)	90	90
β (°)	99.849(5)	100.14(3)
γ (°)	90	90
$V(\text{Å}^3)$	4081.5(9)	4106(9)
Z	8	8
Dc(g·cm ⁻³)	1.258	1.302
$\mu(\text{mm}^{-1})$	0.146	0.151
$F(000)$	1616.0	1680.0
GOF on F^2	1.034	1.016
R_1^a ($I > 2\sigma(I)$)	0.0527(5969)	0.0643(4731)
wR_2^b ($I > 2\sigma(I)$)	0.1450(9407)	0.1438(9499)

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad ^b wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}.$$