Supporting Information

Preparation of Fluorescent Polystyrene Nanoparticles Mediated by Multi-Functional

Amphiphilic Iridium Complex under Visible Light Irradiation in Aqueous

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1. Experimental Section

1.1. Materials

IrCl₃·3H₂O, [Ru(bpy)₃]²⁺, 4-(2-Pyridinyl)benzaldehyde, sodium borohydride, NaH (60% dispersion in mineral oil), 2-ethoxyethanol, phosphorus tribromide and isopropanol were purchased from Aladdin Chemistry Co., Ltd., 2,2'-Bipyridine-4,4'-dicarboxylic Acid was purchased from Zhengzhou Alfachem Co., Ltd., Chloromethyl-4-vinylbenzene and trimethylamine solution (2.0 M solution in THF, water \leq 150 ppm (by K.F.), Mk Seal.) were purchased from Shanghai Macklin Biochemical Co., Ltd. Methyl methacrylate (99%, stabilized with MEHO) and styrene (99.5%, stabilized with HQ) were purchased from J&K China Chemical Ltd (solution was passed through a column of basic alumina before used). All reagents were used directly without any further purification unless stated otherwise. THF was purified by distillation from sodium in the presence of benzophenone. Water deionized with a Millipore system was used in this work.

1.2. Instruments and characterization techniques

Solar light simulator (Oriel 94023A, AAA Class, Newport Corp.) was used to simulate a standard sun illumination (100 mW cm⁻²) identified by a standard silicon solar cell (91150 V,

Newport Corp). ¹H NMR (500 MHz) spectra were recorded on Bruker Advance III. The UVvis spectra were recorded on Genesys 10S Uv-vis spectrophotometer (Thermo Fisher Scientific). High-resolution mass spectra were obtained using Agilent 6500 QTOF-MS spectrometer. Atomic force microscopy (AFM) images were taken by Bruker Multimode 8 instrument with a scan speed of 1 Hz. 10 µL of sample (100 µM) was dropped onto the freshly mica and adsorb for other 3 min at room temperature. Then 200 µL of distilled water was injected into liquid cell and AFM was performed in ScanAsyst in fluid mode. Solid state emission spectra were performed with Hitachi F-4600 spectrofluorometer. Fluorescence lifetime were recorded by DeltaProTM fluorescence lifetime system (Horiba JobinYvon IBH Ltd., Scotland). The droplet/particles size, distribution and Zeta potential were determined by using Malvern Nano ZS-E from Malvern Instruments, Ltd., with a back scattering angle of 173° at 25 °C. Field-emission scanning electron microscope (Nova Nano SEM 230, FE-SEM) and energy dispersive X-ray spectroscopy (EDS) mapping was used to characterize the morphology of particles and distribution of element, by a Hitachi S-4800 scanning electron microscope equipped with an energy dispersive detector. Transmission electron microscopy (FEITecnai G2 F20 TEM) image was conducted with acceleration voltage of 100 kV. Aqueous solution of the sample was deposited onto 200 meshes, holey film, copper grid (ProSciTech) and dried in air before test. Fluorescence images were captured by laser confocal microscopy (Nikon A1) using a channel with an excitation peak of 405 nm.

1.3. Methods

1.3.1. Synthesis of the iridium complex (GIC):

4,4'-bis((4-vinylbenzyloxy)methyl)-2,2'-bipyridine was synthesized according to a previously established procedure^{1, 2}. The detail synthesis procedure was shown as follow:

4-vinylbenzyl acetate (1). Chloromethyl-4-vinylbenzene (1.80 g, 11.8 mmol) and potassium acetate (AcOK) (2.03 g, 20.6 mmol) were added into glacial acetic acid (30mL) and refluxed for 8 h. The mixture was then poured into ice water (10 mL) and extracted with ethyl acetate (50 mL). The organic extracts were washed with NaHCO₃ solution (50 mL) and final dried over with MgSO₄. The solution was removed under reduced pressure to obtain

residue then chromatographed on silica gel with the eluent (hexane : ethyl acetate = 5 : 1) to afford a colorless oil. (1.97 g, 94.4%).

4-vinylbenzyl alcohol (2). To a solution contained with 1 (1.50 g, 9.83 mmol) and KOH (1.94 g, 34.58 mmol) in methanol (9 mL) was added with H₂O (2.7 mL). After the mixture refluxed for 6 h, ice water was introduced and organic phase was extracted with ethyl ether (3 × 50 mL). Then the solvent was removed under reduced pressure to give yellow oil crude product. The crude residue was chromatographed with the eluent (hexane : ethyl acetate = 5 : 1) to obtain a colorless oil (0.95 g, 83%). ¹H NMR (500 MHz, CDCl₃) δ 7.40 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 6.75 (m, *J* = 17.6, 10.9 Hz, 1H), 5.78 (m, *J* = 17.6, 0.7 Hz, 1H), 5.28 (m, *J* = 11.6, 3.4 Hz, 1H), 4.58 (s, 2H).

4,4'-diethtyl ester-2,2'-bipyridine (3). 4,4'-dicarboxy-2,2'-bipyridine (1.5 g, 6.14 mmol) and sulfuric acid (1.5 mL) were added into ethanol (100 mL) and refluxed for 4 days. The solution was cooled to room temperature after react, then the solution was then evaporated. Distilled water was added and use 5 % sodium hydroxide solution to adjust pH to 7. The suspension was filtered and washed with distilled water for 3 times, the white powder product was collected, 4,4'-diethtyl ester-2,2'-bipyridine (1.61 g, 87 %).

4,4'-bis(hydroxymethyl)-2,2'-bipyridine (4). Compound 3 (1.00 g, 3.33 mmol) was added into ethanol (80 mL) contained with sodium borohydride (2.00 g, 52.40 mmol) and refluxed for 4 h. After cooled to room temperature, the solution was evaporated and saturated ammonium chloride solution was added to eliminate excess sodium borohydride, and extracted with ethyl acetate for 3 times to yield 4,4'-bis(hydroxymethyl)-2,2'-bipyridine (0.66 g, 92 %). ¹H NMR (500 MHz, MeOD) δ 8.61 (d, *J* = 5.1 Hz, 2H), 8.29 (d, *J* = 0.7 Hz, 2H), 7.57-7.31 (d, 2H), 4.77 (s, 4H).

4,4'-bis(bromomethyl)-2,2'-bipyridine (5). Compound 4 (0.20 g, 0.93 mmol) was dissolved in 48% hydrobromic acid solution (30 mL) with catalytic sulfuric acid (10 mL) and refluxed for 1 day, then the saturated sodium hydroxide solution was added to adjust pH value at 7. Finally, 4,4'-bi(bromomethyl)-2,2'-bipyridine was given and washed with distilled water for 3 times. (0.27 g, 81%). ¹H NMR (500 MHz, CDCl₃) δ 8.83-8.61 (m, 2H), 8.48 (d, *J* = 1.1 Hz, 2H), 7.47 – 7.36 (m, 2H), 4.51 (s, 4H).

4,4'-bis((4-vinylbenzyloxy)methyl)-2,2'-bipyridine (6). Compound 2 (0.25 g, 1.86 mmol) and NaH (0.20 g) were added to dry THF (10 mL), with mixing for 30 min at RT. Compound 5 (0.30 g, 0.88 mmol) was dissolved in THF (20 mL) and added dropwise to the mixture and refluxed for 18 h to obtain crude product, the residue was purified by silica-gel column chromatography with eluent (hexane : ethyl acetate = 1 : 1) to give white solid. (0.28 g, 72%). ¹H NMR (500 MHz, CDCl₃) δ 8.75 (d, *J* = 4.9 Hz, 2H), 8.58 (s, 2H), 7.55 (s, 2H), 7.45 (d, *J* = 7.9 Hz, 4H), 7.38 (d, *J* = 7.8 Hz, 4H), 6.75 (m, *J* = 17.6, 10.8 Hz, 2H), 5.79 (d, *J* = 17.7 Hz, 2H), 5.29 (d, *J* = 10.9 Hz, 2H), 4.73 (s, 4H), 4.68 (s, 4H).

Pba-4C (9): 4-(2-Pyridinyl)benzaldehyde (0.20 g, 1.10 mmol) and sodium borohydride (0.10 g, 2.65 mmol) were added into ethanol (40 ml) under ice water bath and stirred for 30 min, then transferred to RT for another 2.5 h. The solution was evaporated and saturated sodium carbonate aqueous solution was used to remove excess sodium borohydride before extracted by dichloromethane (3 × 100 mL). Then removed CH₂Cl₂ and the white crude product was obtained [(4-(pyridin-2-yl)phenyl)methanol, (7)]. Subsequently, the residue was dissolved in CH₂Cl₂ (15 mL) and phosphorus tribromide (2 ml) was added dropwise to the mixture at RT and stirred overnight. Saturated sodium carbonate was added to adjust pH=7 and then product was extracted by CH₂Cl₂. The organic phase was removed under residue pressure to obtain white solid [2-(4-(bromomethyl)phenyl)pyridine, (8)]. Next, the solid was dissolved into ethanol (10 ml) and then trimethylamine (2 mL) was added dropwise at RT. After stirring overnight, the solution was evaporated and washed with ethyl ether for three times then centrifuged to give solid for three times to obtain pba-4C (0.31 g, 94%). ¹H NMR (500 MHz, MeOD) δ 8.72 – 8.64 (m, 1H), 8.20 – 8.11 (m, 2H), 7.99 – 7.95 (m, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.48 – 7.42 (m, 1H), 4.65 (s, 2H), 3.19 (s, 9H).

 $[Ir(Pba-4C)_2]_2(\mu-Cl)_2$ (10): Pba-4C (0.20 g, 0.65 mmol) and $IrCl_3 \cdot 3H_2O$ (0.103 g, 0.325 mmol) were dissolved in degassed mixture of 2-ethoxyethanol and H_2O (36 mL, 3:1 v/v). The mixture was then refluxed for 24 h, the solvent was removed under reduce pressure to give crude cyclometalatedIridium(III)-chloride-bridged dimer (0.25 g, 75%).

GIC (11): The cyclometalatedchlorido-bridged dimer 10 (0.15 g, 0.091 mmol) and compound 6 (0.086 g, 0.19 mmol) were added to a degassed mixture of methanol and

dicholoromethane (18 mL, 1:2 v/v). The mixture was refluxed for 12 h in the dark, then solvent was removed under reduce pressure to give the crude product, after recrystallization with distilled water, the deep red solid was obtained (0.10 g, 80%).¹H NMR (500 MHz, MeOD) δ 8.66 (s, 2H), 8.30 (d, *J* = 8.1 Hz, 2H), 8.11 (d, *J* = 7.3 Hz, 2H), 7.75 (d, *J* = 5.6 Hz, 2H), 7.62 (d, J = 5.9 Hz, 3H), 7.47 (s, 4H), 7.44 – 7.37 (m, 8H), 7.24 (m, *J* = 13.5, 6.9 Hz, 4H), 6.99 (s, 2H), 6.75 (d, *J* = 4.9 Hz, 2H), 5.81 – 5.78 (m, 2H), 5.32 – 5.16 (m, 6H), 4.63 (s, 4H), 3.62 (s, 4H), 3.22 (s, 18H). **TOF-MS**: for C₆₀H₆₄IrN₆O₂Br₂⁺ [M-Cl]⁺. Calcd. for: 1251.3100; found, 1251.3056.

1.3.2. Gel Permeation Chromatography (GPC) analysis

Number-average molecular weight (M_n) and dispersities (M_w/M_n) were measured by GPC with refractive index detector (Waters, 2414), using THF as eluent at a flow rate of 1.00 mL/min (45 °C). The GPC system was calibrated with polystyrene standards.

1.3.3. DFT and TDDFT Calculation

All complexes were modeled using Gaussian 16 A03 program package, using the following DFT protocol at the B3LYP level of theory with the def-SVP for C, H, O, N atoms, and LANL2DZ basis set for iridium atom. For geometries in the excited states calculation was using m06-2x level of theory with the SDD basis set for iridium atom and def-TZVP for other atoms. Using Marcus Equation (eq. S1) to justify the electron transition rate between singlet states and triplet states.³ Equation S2 (eq. S2) shows legible to judge the rate of ISC, the higher value of the coefficient δ , the greater ISC rate of complexes.

$$K_{ISC} = \frac{2\pi}{\hbar} \langle {}^{1}\Psi_{S}^{0} | H_{SO} | {}^{3}\Psi_{S}^{0} \rangle^{2} \frac{1}{\sqrt{4\pi\lambda RT}} exp\left[-\frac{\left(\lambda + \Delta E_{ST}\right)^{2}}{4\lambda RT} \right]$$
Equation
S1

 $\delta = \frac{\left\langle \Psi_{S} \right| H_{SO} \left| \Psi_{T} \right\rangle}{\Delta E_{ST}}; k_{ISC} \propto \delta^{2}$

Equation S2

(δ represents the coefficient.)

1.3.3. Light-mediated polymerization processes

Typically, GIC (6 mg, 0.0046 mmol), styrene (1 mL) and distilled water (4 mL) were added into Pyrex tube, purged with nitrogen for 15 minutes, then polymerization processes was carried out *via* exposing the reaction mixture to simulated sunlight. The reactions were stopped by turning off the light. To detect the morphology of GIC/Ps, the latex was dripped onto the petri dish, kept at room temperature for about 1 day, and then observed by SEM and TEM. The monomer conversions were obtained by gravimetric measurement according to previous method with minor change. After completion of the polymerization, 1 mL aliquot was transferred to a weighed glass vial and reweighed. After drying overnight in a vacuum oven at 35 °C, the residues were washed with methanol, and then dried at 35 °C overnight under vacuum. The final product was reweighed and the conversion of monomer calculated based on the solution composition.⁴

$$Conversion (\%) = \frac{m_{polymer}}{m_0} \times 100\%$$

 $m_{polymer}$ stands for the final mass of polymer after washing with methanol (g), m_0 stands for the initial mass of monomer (g).



Scheme S1. Synthetic procedure of complex GIC

2. ¹H NMR spectra for compounds



Figure S1. ¹H NMR spectrum of 4-vinylbenzyl alcohol (2) in CDCl₃.



Figure S2. ¹H NMR spectrum of 4,4'-bis(hydroxymethyl)-2,2'-bipyridine (4) in MeOD.



Figure S3. ¹H NMR spectrum of 4,4'-bis(bromomethyl)-2,2'-bipyridine (5) in CDCl₃.



Figure S4. ¹H NMR spectrum of 4,4'-bis((4-vinylbenzyloxy)methyl)-2,2'-bipyridine(6) in CDCl₃.



Figure S5. ¹H NMR spectrum of Pba-4C (9) in MeOD.



Figure S6. ¹H NMR spectrum (in MeOD) and TOF-MS spectrum of GIC (11).

3. Time-resolved luminescence decay spectrum of GIC



Figure S7. Time-resolved luminescence decay curves of GIC in aqueous solution at room temperature.

4. Pictures of latex



Figure S8. Digital images of the latex without (a) and with (b) UV light (365nm).

5. Morphology analysis of GIC/Ps



Figure S9. FESEM (a) and TEM image (b) of GIC/Ps.

6. Uv-vis and FT-IR spectrum analysis



Figure S10. (a) The absorption spectra of GIC and GIC/Ps.; (b) The FT-IR spectra of GIC and GIC/Ps.

7. TGA curve of the GIC/Ps particles.



Figure S11. TGA curve of GIC/Ps.

8. Time-resolved luminescence decay spectrum of GIC and GIC/Ps



Figure S12. Time-resolved luminescence decay curves at solid states of GIC and GIC/Ps.

9. Comparison of GIC/Ps with different concentration of GIC.



Figure S13. DLS and GPC traces of GIC/Ps with different amount of GIC (0.001 g for (a) and (b), and 0.006 g for (c) and (d)).



10. HOMO and LUMO energy levels and electron distributions of GIC and GIC/St.

Figure S14. The electron distribution based on the optimization of the ground state for GIC before (GIC) and after interacted with styrene (GIC/St).

11. Electron distribution of GIC and visible light induced polymerization mechanism.



Scheme S2 (a) The electron distribution of the complex in T1 state interacted with styrene under optimal conformational condition (The red area marked in the graph is the unpaired electron distribution region.), (b) the possible mechanism for visible light mediated polymerization of styrene.

12 Table S1. Properties of GIC under aqueous solution

$\lambda_{abs} [nm]$	$\lambda_{em} [nm]$	Φ_{p}^{-a}	τ ^b [ns]	$k_r c [s^{-1}]$	$k_{nr} d[s^{-1}]$
253, 314, 430, 460.	560	0.017	201.07	0.17×10^{3}	4.89×10^{3}

^a Φ_p refers to the photoluminescence quantum yield, which used $[Ru(bpy)_3]^{2+}$ as standard ($\Phi_p = 0.028$ in water);

^b lifetime data: excitation wavelength 365 nm;

^{c, d} k_r and k_{nr} values in solution were calculated using the equations: $k_r = \Phi/\tau$ and $k_{nr} = (1 - \Phi)/\tau$.

13. Table S2. The state of polymerization under different conditions.

#	Condition	Polymerization state observed by naked	Precipitation in
# Condition"		eyes after 10 hours	Methanol
1	Light, GIC, St, H ₂ O	milky-like with stability of emulsion	white
			precipitation
2	GIC, St, H ₂ O	transparent solution	n.d. ^b
_3	Light, St, H ₂ O	transparent solution	n.d. ^b

^a The mixture was purged with nitrogen for 15 minutes before reaction;

^b n.d. = not observed by naked-eyes.

14. Table S3. Analytical data for GIC/Ps.

	Yield (%)	$M_{ m w}{}^{ m a}$	$M_{ m w}/M_{ m n}^{ m a}$
GIC/Ps	60	321000	2.0

^a The values are measured by GPC.

15. Table S4. Spin orbit coupling matrix elements of iridium(III) complex.

(S_n, T_m)	$<$ Sn $ H_{SO} $ Tm $>$ (cm ⁻¹)	$\Delta E_{ST} (eV)$	δ
(4,2)	30.3	0.0163	1859
(2,4)	30.1	0.1008	299
(4,1)	21.1	0.1670	126
(1,4)	20.9	0.1664	126
(2,1)	12.9	0.0734	175
(1,2)	12.9	0.0726	178

Spin orbit coupling matrix elements was calculated according to previous reported.⁵

16. Reference:

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