Electronic Supplementary Information

Efficient synergistic photocatalysis of supported Ir/Pd dual

metal catalysts based on flexible polymeric brushes

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1. Preparation procedures for raw materials

1.1 PVBC@SiO₂



Fig.S1 Preparation route to PVBC@SiO₂.

1.1.1 NH₂@SiO₂

To a two-necked flask (250 mL), anhydrous ethanol (110 mL) and ammonia (5.7 mL, 28 wt%) were added, heated to 35 °C. Then, a solution of ethanol (7.8 mL) containing tetraethyl orthosilicate (TEOS, 3.8 mL) was added to the system with a peristaltic pump (1.2 mL min⁻¹). After 24 h, 3-(azidopropyl)triethoxysilane (APTES, 2.4 mL) was added dropwise (1.0 mL min⁻¹) and stirred for another 12 h. The reaction mixture was cooled to room temperature and centrifuged by centrifugation $(1.3 \times 10^4 \text{ rpm}, 5 \text{ min})$. The solid was washed by anhydrous ethanol (50 mL × 3) and dried at 45 °C for 6 h to obtain white solid powder (NH₂@SiO₂) (1.20 g).



Fig.S2 SEM image (left) and particle size distribution (right) of NH₂@SiO₂.

1.1.2 CPDB@SiO₂

In a Ar-filled dry three-necked flask (50 mL), NH₂@SiO₂ (1.0 g) was dispersed in THF (10 mL)

at room temperature for 6 h, and a THF suspension (10 mL) containing 4-cyano-4- [(phenylcarbonothioyl)sulfanyl]pentanoic acid (CPDB, 200 mg, 0.54 mmol) was added and stirred at 25 °C for 24 h. Subsequently, a cyclohexane/ether mixture (50 mL, $V_1/V_2 = 4/1$) was added, and the solid was centrifuged at 1.0×10^4 rpm for 2 min. The isolated solid was stirred in THF (15 mL) to afford a suspension, and then precipitated again with a mixed solvent of cyclohexane/ether (50 mL, v/v= 4/1), followed by centrifugation at 1.0×10^4 rpm for 2 min. This procedure was repeated until the centrifugate became colorless and transparent. The solid was dried at 35 °C under vacuum for 6 h, yielding a light pink solid powder (CPDB@SiO₂) (890 mg).



1.1.3 PVBC@SiO₂ including PVBC(L)@SiO₂ and PVBC(S)@SiO₂

Fig.S3 SEM images and particle size distributions of $Pd\&Ir#PVBC(S)@SiO_2(a)$ and $Pd\&Ir#PVBC(L)@SiO_2(b)$.

To a dry Schlenk tube (25 mL), CPDB@SiO₂ (350 mg) in THF (4.0 mL) was added and dispersed by sonication (300 W, 40 kHz) for 5 min, affording a well-dispersed suspension. THF solution (270 μ L, 0.05 mol L⁻¹) containing AIBN (8.3 mg), 4-vinyl benzyl chloride (VBC, 2.5 g, 18.04 mmol) were added and dispersed by sonication (300 W, 40 kHz) for 5 min. The resulting suspension was frozen by liquid N₂ into solid and then evacuated at room temperature using oil pump till the solid completely melted into to a suspension. This freeze-pump-thaw cycle was repeated twice. The reaction mixture was warmed naturally to room temperature, filled by N₂, sonicated for 10 min, and stirred at 80 °C for 18 h. After being cooled to 25 °C in an ice bath, the solid was isolated by centrifugation (1.0×10^4 rpm, 5 min), washed by THF (9 mL × 3), dried under vacuum at 75 °C for 6 h, and milled to light yellow solid powder (PVBC(S)@SiO₂, 385 mg) with a PVBC chain length of $M_n = 1.97 \times 10^4$ and the -CH₂Cl content of 0.95 mmol g⁻¹. When the reaction time was prolonged to 36 h, the light yellow solid powders (PVBC(L)@SiO₂, 432 mg) with a longer

PVBC chain length of $M_n = 2.68 \times 10^4$ and a -CH₂Cl content of 1.28 mmol g⁻¹ were obtained according to the same procedure as PVBC(S)@SiO₂.

1.2 Hollow mesoporous polystyrene nanospheres (HMPNs)



Fig.S4 Preparation route to HMPNs.

1.2.1. Polystyrene nanospheres (PS)

In an Ar-filled three-necked flask (500 mL), styrene (8.20 g, 0.08 mmol), polyvinylpyrrolidone (PVP, 1.65 g, 0.03 mmol) and distilled water (180 mL) were charged. The mixture was stirred at room temperature for 20 min. KPS (0.45 g, 1.67 mmol) dissolved in distilled water (9 mL) was added, stirred at room temperature for 20 min, and heated to 85 °C for 24 h. The reaction mixture was centrifuged at 1.3×10^4 rpm for 5 min, and the solid was washed with deionized water (20 mL × 3) and anhydrous ethanol (20 mL × 3). The product was dried at 40 °C to obtain white polystyrene nanospheres (PS, 6.20 g).



Fig.S5 SEM image (left) and particle size distribution (right) of PS.

1.2.2. Hollow mesoporous nanospheres (HMPNs)

PS (400 mg) was dispersed in an aqueous polyvinyl alcohol (PVA) solution (20 mL, 0.5 wt%) at 25 °C for 24 h to prepare an emulsion of PS. Under Ar atmosphere, a three-necked flask (150 mL) was charged with an aqueous PVA solution (20 mL, 0.5 wt%), F127 (0.5 g, 0.04 mmol), *p*-vinyl benzyl chloride (VBC, 153 mg, 1.0 mmol) and styrene (208 mg, 2.0 mmol). The mixture was stirred at 25 °C for 20 min, followed by the addition of the aforementioned PS emulsion. The mixture was stirred at 25 °C for 4 h. Subsequently, KPS aqueous solution (8 mL, 70 mg, 0.26 mmol) was added, stirred for 10 min, heated to 65 °C and allowed to react for 80 min. Subsequently,

styrene (104 mg, 1.0 mmol), divinylbenzene (DVB, 120 mg, 1.0 mmol), and VBC (153 mg, 1.0 mmol) were added and heated to 75 °C for 24 h. After being cooled, the solid was centrifuged (1.3×10^4 rpm, 5 min) and washed with distilled water (20 mL × 3) and anhydrous ethanol (20 mL) until the centrifugate was colorless and clear. The solid was stirred at 25 °C in a mixed solvent of THF and EA (v/v = 1:1) for 6 h and centrifuged (1.0×10^4 rpm, 5 min). The isolated solid was stirred at 65 °C in a mixed solvent of EA and acetone (v/v = 1:1) for 12 h, followed by centrifugation (1.0×10^4 rpm, 5 min). The obtained solid was dried at 40 °C to afford white HMPNs (0.35 g).



Fig.S6 SEM image (left) and particle size distribution (right) of HMPNs.

2. Methods for determining important parameters

2.1 M_n and PDI of PVBC brushes

In N₂-filled dry three-necked flask (100 mL), PVBC@SiO₂ (250 mg) and an anhydrous ethanol solution (50 mL) containing NH₄I (150 mg) were added. The system was evacuated, filled with N₂, subjected to ultrasonic dispersion for 2 h, heated to 75 °C for 2 h. To the well-mixed suspension, N₂H₄·H₂O (500 mg) was added and stirred at 75 °C for 24 h. After being cooled to 25 °C, the solid was centrifuged (1.0×10^4 rpm, 5 min), washed by THF (5 mL × 3). The centrifugate was combined, added with distilled water (150 mL) and extracted by CHCl₃ (20 mL × 3). The combined organic phases were filtered through 0.22 µm filter, and evaporated to afford pale yellow viscous oil. The molecular weights (M_n) and polymer dispersity indexes (PDI) were determined by using Waters gel-permeation chromatograph (GPC).

2.2 Loading amount of benzyl chloride moieties

HMPNs (300 mg) in THF (2 mL) was added to a round-bottomed flask (25 mL) and dispersed by ultrasonication for 10 min. Aqueous NaOH solution (5 mL, 1.0 mol L⁻¹) was added, and the reaction was carried out for 12 h at 40 °C and filtered. The obtained supernatant was evaporated to remove THF, filtered using filter head (0.22 μ m). Dilute HNO₃ (0.1 mol L⁻¹) was added to pH = 7 and aqueous K₂CrO₄ (1 mL, 0.5 wt%) was added. The aqueous solution was titrated with standard aqueous AgNO₃ solution (0.1 mmol mL⁻¹) and repeated twice. The average value (7.26 mL) was used to calculate the amount of -CH₂Cl in HMPNs to be 2.42 mmol g⁻¹. According to the same procedure, the amounts of -CH₂Cl in PVBC(L)@SiO₂ and PVBC(S)@SiO₂ were determined to be 1.28 mmol g⁻¹ and 0.95 mmol g⁻¹, respectively.

3. Characterization

¹H NMR spectra were acquired on Bruker av-600 NMR instrument, in which all chemical shifts were reported down-field in ppm relative to the hydrogen resonances of TMS. Solid-state ¹³C and ³¹P CP/MAS NMR spectra were acquired on Bruker Avance Neo 400WB spectrometer at the resonance frequencies of 150.7 MHz for ¹³C and 161.9 MHz for ³¹P using the cross-polarization (CP), magic-angle spinning (MAS), and a high-power ¹H decoupling. Scanning electron microscopy (SEM) images were observed by a Sigma 300 instrument operating at 10.0-25.0 kV, and the samples should be coated with a thin layer of gold before testing. Transmission electron microscopy (TEM) images were obtained on a FEI Tecnai F20 instrument operated at 200 kV. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to determine the loading capacities of Pd and Ir on Agilent 5110 instrument. Thermogravimetric analysis (TGA) was conducted on a Thermo plus EVO2. X-ray photoelectron spectroscopy (XPS) was recorded on a Thermo Scientific K-Alpha instrument with Al K α irradiation at θ = 90° for X-ray source, and the binding energy was calibrated through the reference of C1s (284.9 eV). Molecular weights and molecular weight distributions of PVBC brushes were quantitated by a Waters gel-permeation chromatograph (GPC) on a PL-GPC220 instrument. Fourier Transform infrared spectroscopy (FT-IR) spectra were acquired on a Perkin-Elmer Spectrum GX instrument using KBr pellet. N2 adsorption-desorption isotherms were obtained at 77.4 K on QUADRASORB SI instrument.

3.1 Thermogravimetric analysis



Fig.S7 Thermogravimetric curves of PVBC@SiO₂ with different chain lengths.

3.2 Grafting density of PVBC brushes (σ)

The grafting density of PVBC can be calculated by the following formula:

$$\sigma = \frac{(1 - f_{sio2})N_A \rho_{sio2} \alpha}{6 f_{sio2} M_n}$$

Where f_{SiO2} is the mass fraction of SiO₂ measured by TGA, N_A is the Avogadro number, ρ_{SiO2} is the density of SiO₂ NPs (2.2 g cm⁻³), and *d* is the average diameter of SiO₂ NPs.

3.3 Morphology and particle size



Fig.S8 SEM image (left) and particle size distribution (right) of Pd&Ir#HMPNs.



Fig.S9 SEM images and particle size distributions of Pd&Ir#PVBC(S)@SiO₂(a) and Pd&Ir#PVBC(L)@SiO₂(b).



Fig.S10 TEM images of PVBC(L)@SiO₂ (a) and Pd&Ir#PVBC(L)@SiO₂(b), and TEM-EDS mappings of Pd&Ir#PVBC(L)@SiO₂(c).

3.4 CP/MAS ³¹P NMR



Fig.S11 CP/MAS ³¹P NMR spectrum of PVBC(L)@SiO₂-supported single PPh₃.



3.5 N₂ adsorption-desorption isotherm

Fig.S12 N₂ adsorption-desorption isotherm and pore size distribution of Pd&Ir@HMPNs.

4. One-pot immobilization of Pd (PPh₃)₄ and Ir(ppy₂)(dtbbpy)PF₆

To an dry flask (50 mL) equipped with a magnetic stir bar, $Pd(PPh_3)_4$ (115.6 mg, 0.10 mmol), $Ir(ppy_2)(dtbbpy)PF_6$ (36.6 mg, 0.04 mmol), $PVBC(S)@SiO_2$ (134.7 mg), and dried 1, 2-dichloroethane (DCE, 10 mL) were added. The resulting mixture was stirred at 25 °C for 3 h in an argon atmosphere. A DCE solution (5 mL) containing FeCl₃ (11.4 mg, 0.07 mmol) was added by

using syringe, heated to 60 °C for 30 h. After the reaction mixture was cooled naturally to room temperature, the solids were isolated by centrifugation $(1.0 \times 10^4, 3 \text{ min})$, washed with hydrochloric acid (2.0 mol L⁻¹, 20 mL × 3) and ethanol (20 mL), dried at 60 °C for 8 h under reduced pressure to afford yellowish-brown PVBC brush-supported dual Pd/Ir complexes (174 mg) (Pd&Ir#PVBC(S)@SiO₂). According to the above-mentioned procedure, PVBC(L)@SiO₂ (100 mg) and HMPNs (53 mg) with the same content of -CH₂Cl moieties as PVBC(S)@SiO₂ are used as catalyst supports to afford corresponding Pd&Ir@HMPNs (123.5 mg) and Pd&Ir#PVBC(L)@SiO₂ (151 mg), respectively.

In the above-mentioned immobilization procedure, the samples are taken by syringe every 3 hours. The taken sample (5 uL) is diluted by CH_3CN , filtered by filter head, and further diluted to constant volume (1 mL). The contents of $Pd(PPh_3)_4$ and $Ir(ppy_2)(dtbbpy)PF_6$ are quantitatively determined by HPLC (Fig.S13⁺). The loading capacities of dual catalysts are listed in Table S1 and Table S2.



Fig.S13 HPLC spectrum of the reaction mixture in the one-pot immobilization of Pd(PPh₃)₄ and Ir(ppy₂)(dtbbpy)PF₆ into PVBC(L)@SiO₂ (S₁: peak of Pd(PPh₃)₄, S₂: peak of Ir(ppy₂) (dtbbpy)PF₆) (HPLC conditions: V_{CH3OH}/V_{H2O} = 96:4, 0.3 mL min⁻¹, C18 column, 25 °C).



Fig.S14 HPLC spectrum of Pd(PPh₃)₄ in DCE containing FeCl₃ at 60°C for 10 h (HPLC conditions: $V_{CH3OH}/V_{H2O} = 96:4$, 0.3 mL min⁻¹, C18 column, 25 °C).



Fig.S15 Standard curve of Pd (PPh₃)₄(left) and Ir(ppy₂) (dtbbpy)PF₆(right).

Table S1 Residual and loaded amounts of $Pd(PPh_3)_4$ and $Ir(ppy_2)(dtbbpy)PF_6$ during whole immo-bilization process obtained from $HPLC^a$

Sample		PVBC(S))@SiO ₂	-		PVBC(L)@SiO ₂	
	${\sf R}_{\sf Pd}^{\sf b}$	L_{Pd}^{c}	R_{lr}^{d}	L _{Ir} e	R_{Pd}^{b}	L _{Pd} ^c	R_{lr}^{d}	L _{Ir} e
Time(h)	(mmol)	(mmol g ⁻¹	(mmol)	(mmol g ⁻¹	(mmol)	(mmol g ⁻¹	(mmol)	(mmol g ⁻¹
		PVBC)		PVBC)		PVBC)		PVBC)
0	0.100	0	0.040	0	0.100	0	0.040	0
3	0.091	0.451	0.037	0.175	0.089	0.555	0.035	0.242
6	0.085	0.788	0.035	0.267	0.080	1.009	0.032	0.404
9	0.077	1.178	0.031	0.437	0.073	1.359	0.028	0.610
12	0.072	1.424	0.028	0.605	0.067	1.684	0.025	0.748
15	0.066	1.748	0.026	0.694	0.060	2.034	0.024	0.835
18	0.063	1.904	0.024	0.820	0.056	2.241	0.022	0.930
21	0.061	1.982	0.023	0.872	0.052	2.436	0.020	1.019
24	0.059	2.099	0.022	0.924	0.051	2.527	0.019	1.057
27	0.058	2.151	0.021	0.966	0.050	2.553	0.018	1.107
30	0.057	2.190	0.021	0.990	0.050	2.579	0.018	1.144

^a Conditions: Pd(PPh₃)₄ (115.6 mg, 0.10 mmol), Ir(ppy₂)(dtbbpy)PF₆ (36.6 mg, 0.04 mmol), PVBC(S)@SiO₂(134.7 mg), PVBC(L)@SiO₂ (100 mg), 60 °C, 30 h; ^b The residual amounts of Pd(PPh₃)₄ in DCE solution; ^c The loaded amounts of Pd(PPh₃)₄ in PVBC@SiO₂ ; ^d The residual amounts of Ir(ppy₂)(dtbbpy)PF₆ in DCE solution; ^e The loaded amounts of Ir(ppy₂)(dtbbpy)PF₆ in PVBC@SiO₂.

Table S2 Residual and loaded amounts of Pd(PPh₃)₄ and Ir(ppy₂)(dtbbpy)PF₆ during whole immo-

bilization process obtained from HPLC^a

Sample	PVBC(L)@SiO ₂				
	R _{Pd} ^b	L _{Pd} ^c	R _{ir} ^d	L _{Ir} ^e	
Time(h)	(mmol)	(mmol g ⁻¹ PVBC)	(mmol)	(mmol g ⁻¹ PVBC)	
0	0.100	0	0.040	0	
3	0.091	0.477	0.036	0.202	
6	0.084	0.840	0.035	0.273	
9	0.079	1.087	0.034	0.308	

12	0.074	1.307	0.033	0.377
15	0.073	1.372	0.032	0.401
18	0.072	1.450	0.031	0.458
21	0.071	1.502	0.031	0.467
24	0.070	1.515	0.031	0.472
27	0.070	1.528	0.031	0.478
30	0.070	1.528	0.031	0.478

^a Conditions: Pd(PPh₃)₄ (115.6 mg, 0.10 mmol), Ir(ppy₂)(dtbbpy)PF₆ (36.6 mg, 0.04 mmol), PVBC(L)@SiO₂ (100 mg), 70 °C, 30 h; ^b The residual amounts of Pd(PPh₃)₄ in DCE solution; ^c The loading amounts of Pd(PPh₃)₄ in PVBC(L)@SiO₂; ^d The residual amounts of Ir(ppy₂)(dtbbpy)PF₆ in DCE solution; ^e The loading amounts of Ir(ppy₂)(dtbbpy)PF₆ in PVBC(L)@SiO₂.

Table S3 Properties of Pd&Ir#PVBC(L)@SiO₂ (Cat.A), Pd&Ir#PVBC(S)@SiO₂ (Cat.B), and

Parameter	Cat.A	Cat.B	Cat.C			
Pd (wt%)	4.76 [°]	2.99 ^a	6.15 ^ª			
Pd (mmol g^{-1})	0.45 [°]	0.28 ^a	0.58 ^ª			
Pd (mmol g ⁻¹ PVBC)	2.29 ^ª /2.58 ^b	1.94 ^a /2.19 ^b	1.57 ^a			
lr (wt%)	3.68 ^ª	2.26 ^a	4.52 ^a			
Ir (mmol g ⁻¹)	0.19	0.12	0.24			
Ir (mmol g ⁻¹ PVBC)	0.98 ^a /1.14 ^b	0.81 ^a /0.99 ^b	0.64 ^a			
M_n of PVBC ^c	2.68×10 ⁴	1.97×10 ⁴	-			
PDI of PVBC ^c	1.91	1.85	-			
δ (nm ⁻²)	0.39	0.43	-			
^a Determined by ICP-OES. ^b Determined by HPLC. ^c Determined by GPC.						

Pd&Ir@HMPNs (Cat.C)

5. α -Allylation

5.1 General procedure

To a dry Schlenk tube (10 mL) equipped with a magnetic stir bar, Pd&Ir#PVBC(L)@SiO₂(33.6 mg, 5.0 mol% Pd, and 2.1 mol% Ir) was added. After being alternately deaerated and aerated in Ar atmosphere three times, cinnamyl acetate (52.8 mg, 0.3 mmol), *N*-phenyl-1,2,3,4- tetrahy-droisoquinoline (75.3 mg, 0.36 mmol) and dried CH₃CN (2 mL) were charged. The resulting mixture was stirred at room temperature under the irradiation of LEDs (blue, 3W, 460 nm) for 40 h. After being isolated by centrifugation the catalyst was recovered, washed with ethanol, dried naturally and directly reused in the following cycles. The centrifugate was distilled under reduced pressure, and the residue was purified by flash chromatography on silica gel (petroleum ether/DCM = 6/1) to afford pure amine product.

5.2 Reaction dynamics

In the above-mentioned α -allylation of *N*-phenyl-1,2,3,4-tetrahydroisoquinoline with cinnamyl acetate, the samples are taken by syringe every 4 hours. The taken sample (5 uL) is diluted by CH₃CN, filtered by filter head, and further diluted to constant volume (1 mL). The contents of product are quantitatively determined by HPLC (Fig.S16[†]), and the yields of the product are listed in Table S4.



Fig.S16 HPLC spectrum of the α -allylation of *N*-phenyl-1,2,3,4-tetrahydroisoquinoline by cinnamyl acetate (S₁: peak of cinnamyl acetate, S₂: peak of *N*-phenyl-1,2,3,4-tetrahydroisoquinoline, P: peak of product (rate: 0.5 mL min⁻¹, V_{CH3CN}/V_{H2O} = 80:20, C18 column, 25 °C).



Fig.S17 Correlation curve of product concentration and peak area



tained from HPLC^a

Sample Yield(%) Time(h)	Pd(PPh ₃) ₄ +Ir(pp y) ₂ (dtbbpy)PF ₆	Pd&Ir#PVBC(L) @SiO ₂	Pd&Ir#PVBC(S) @SiO ₂	Pd&Ir@HMPNs
4	18.4	16.1	13.1	10.7
8	32.8	30.1	25.5	21.5
12	47.6	44.4	36.0	32.0
16	60.6	56.0	45.3	40.5

20	69.0	65.7	52.8	47.7
24	75.3	71.5	59.4	54.3
28	78.0	75.5	64.7	58.7
32	79.8	77.9	68.8	61.1
36	80.3	78.4	70.6	62.6
40	80.4	78.4	71.0	62.9

^a Reaction conditions: cinnamyl acetate (52.9 mg, 0.30 mmol), *N*-phenyl-1,2,3,4-tetrahydroisoquinoline (75.3 mg, 0.36 mmol), solvent (2 mL), Cat. (5 mol% of Pd), LEDs (blue light, 3W, 460 nm), r.t., Ar.

5.3 Condition optimization

The α -allylation of *N*-phenyl-1,2,3,4-tetrahydroisoquinoline by cinnamyl acetate is selected as a model reaction to investigate the catalytic performance of Pd&Ir#PVBC(L)@SiO₂. Various reaction conditions, including solvent, reaction time, catalyst loading and light source, are optimized and shown in Table S5. Solvent screening (Entries 1–8) indicates that CH3CN is proved to be the optimal reaction medium. The corresponding product is produced at room temperature in 78% yield under the irradiation of blue light (3W) in the presence of 5 mol% of Pd(PPh₃)₄ and 2.1 mol% of Ir(ppy)₂(dtbbpy)PF₆ within 40 h (Entry 5). Unfortunately, the yields of the product are not improved in the further optimizations of reaction time (Entries 14,15), catalyst loading (Entries 9,10), light source (Entries 12,13) and light power (Entries 16,17). Moreover, the reaction does not proceed in the absence of light, and no product is obtained (Entry 11).

Table S5 Condition optimization for the α -allylation of *N*-phenyl-1,2,3,4-tetrahydroisoquinoline by cinnamyl acetate catalysed by Pd&Ir#PVBC(L)@SiO₂^a



Entry	Solvent	Time(h)	Pd/lr(mol%) ^b	Light	Power(W)	Yield(%) ^c
1	Toluene	40	5/2.1	Blue	3	11
2	DCM	40	5/2.1	Blue	3	48
3	Et ₂ O	40	5/2.1	Blue	3	N.D.
4	Acetone	40	5/2.1	Blue	3	21
5	CH₃CN	40	5/2.1	Blue	3	78
6	MeOH	40	5/2.1	Blue	3	65

7	DMF	40	5/2.1	Blue	3	23
8	DCE	40	5/2.1	Blue	3	37
9	CH₃CN	40	2/0.8	Blue	3	50
10	CH₃CN	40	10/4.2	Blue	3	78
11	CH₃CN	40	10/4.2	-	-	0
12	CH₃CN	40	5/2.1	White	3	67
13	CH₃CN	40	5/2.1	Purple	3	60
14	CH₃CN	20	5/2.1	Blue	3	66
15	CH₃CN	60	5/2.1	Blue	3	76
16	CH₃CN	40	5/2.1	Blue	6	60
17	CH ₃ CN	40	5/2.1	Blue	9	52

^a Reaction conditions: Cinnamyl acetate (52.9 mg, 0.30 mmol), *N*-phenyl-1,2,3,4-tetrahydro-isoquinoline (75.3 mg, 0.36 mmol), solvent (2 mL), Pd&Ir#PVBC(L)@SiO₂ (33.6 mg) containg 5 mol% Pd and 2.1 mol% Ir, LEDs (blue: 460 nm, white: 400–800 nm, purple: 365 nm) r.t., Ar. ^b The used amounts of Pd(PPh₃)₄ and Ir(ppy)₂(dtbbpy)PF₆ anchored in Pd&Ir#PVBC(L)@SiO₂. ^c Yield obtained by HPLC. N.D.: not detected.

5.4 Proposed mechanism of homogeneous-like α -allylation



Fig.S18 Possible mechanism of homogeneous-like catalysis catalysed by Pd&Ir#PVBC@SiO2.

6. ¹H NMR spectra of products



Yield: 88 %,¹ Light yellow powder; ¹H NMR (600 MHz, CDCl₃) δ 7.22 (t, J = 7.9 Hz, 2H), 7.13 – 7.06 (m, 4H), 6.92 (d, J = 7.9 Hz, 2H), 6.76 (t, J = 7.1 Hz, 1H), 4.34 (s, 2H), 3.49 (t, J = 5.8 Hz, 2H), 2.92 (t, J = 5.6 Hz, 2H).





Yield: 65 %,¹ Light yellow powder; ¹H NMR (600 MHz, CDCl₃) δ 7.12 – 7.03 (m, 4H), 6.92 – 6.82 (m, 4H), 4.24 (s, 2H), 3.39 (t, *J* = 5.8 Hz, 2H), 2.89 (t, *J* = 5.7 Hz, 2H).





Yield: 50 %,¹ Light yellow powder; ¹H NMR (600 MHz, CDCl₃) δ 7.11 (m, J = 24.7, 15.6, 8.1 Hz, 6H), 6.81 (d, J = 8.8 Hz, 2H), 4.30 (s, 2H), 3.46 (t, J = 5.8 Hz, 2H), 2.91 (t, J = 5.7 Hz, 2H).





Yield: 63 %,¹ Brown powder; ¹H NMR (600 MHz, CDCl₃) δ 7.11 – 7.03 (m, 4H), 7.01 (d, *J* = 8.3 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 4.27 (s, 2H), 3.42 (t, *J* = 5.8 Hz, 2H), 2.89 (t, *J* = 5.8 Hz, 2H), 2.19 (s, 3H).





Yield: 78 %,² light yellow oil; ¹H NMR (600 MHz, CDCl₃) δ 7.19 (dd, *J* = 15.1, 6.1 Hz, 6H), 7.10 (dt, *J* = 17.0, 7.9 Hz, 5H), 6.85 (d, *J* = 7.5 Hz, 2H), 6.68 (t, *J* = 6.7 Hz, 1H), 6.31 (d, *J* = 15.8 Hz, 1H), 6.18 – 6.05 (m, 1H), 4.75 (t, *J* = 6.6 Hz, 1H), 3.56 (m, *J* = 17.7, 9.8, 5.6 Hz, 2H), 3.02 – 2.91 (m, 1H), 2.82 (dd, *J* = 20.0, 12.4 Hz, 2H), 2.58 (dt, *J* = 14.2, 7.2 Hz, 1H).





Yield: 67 %,² light yellow oil; ¹H NMR (600 MHz, CDCl₃) δ 7.18 – 7.01 (m, 6H), 6.81 (d, J = 8.3 Hz, 2H), 6.65 (t, J = 7.2 Hz, 1H), 5.81 – 5.73 (m, 1H), 4.97 (t, J = 12.9 Hz, 2H), 4.66 (t, J = 6.8 Hz, 1H), 3.59 – 3.47 (m, 2H), 2.97 – 2.89 (m, 1H), 2.79 (dt, J = 15.9, 5.3 Hz, 1H), 2.65 (dt, J = 13.9, 6.8 Hz, 1H), 2.41 (dt, J = 14.3, 7.2 Hz, 1H).





Yield: 58 %,² light yellow oil; ¹H NMR (600 MHz, CDCl₃) δ 7.16 (t, *J* = 7.9 Hz, 2H), 7.10 – 7.00 (m, 4H), 6.81 (t, *J* = 7.6 Hz, 2H), 6.65 (dd, *J* = 9.3, 5.1 Hz, 1H), 5.42 – 5.32 (m, 2H), 4.62 (q, *J* = 7.2 Hz, 1H), 3.59 – 3.46 (m, 2H), 2.94 (m, *J* = 13.5, 7.8, 5.6 Hz, 1H), 2.86 – 2.78 (m, 1H), 2.63 – 2.55 (m, 1H), 2.45 – 2.30 (m, 1H), 1.94 – 1.74 (m, 2H), 1.27 (dd, *J* = 14.7, 7.3 Hz, 2H), 0.81 – 0.75 (m, 3H).





Yield: 80 %,² light yellow oil; ¹H NMR (600 MHz, CDCl₃) δ 7.10 (m, *J* = 23.6, 18.3, 12.6, 6.8 Hz, 9H), 6.85 – 6.78 (m, 2H), 6.71 (dd, *J* = 9.2, 4.5 Hz, 2H), 6.42 (d, *J* = 11.7 Hz, 1H), 5.68 (dt, *J* = 11.7, 7.3 Hz, 1H), 4.58 (t, *J* = 6.9 Hz, 1H), 3.48 – 3.39 (m, 2H), 2.93 – 2.79 (m, 2H), 2.73 – 2.64 (m, 2H).





Yield: 61 %,² light yellow oil; ¹H NMR (600 MHz, CDCl₃) δ 7.22 – 7.03 (m, 12H), 6.67 (d, *J* = 9.0 Hz, 2H), 6.44 (d, *J* = 11.7 Hz, 1H), 5.66 (dt, *J* = 11.7, 7.4 Hz, 1H), 4.63 (t, *J* = 7.0 Hz, 1H), 3.50 – 3.39 (m, 2H), 2.94 – 2.81 (m, 2H), 2.76 – 2.66 (m, 2H).





Yield: 60 %,² light yellow oil; ¹H NMR (600 MHz, CDCl₃) δ 7.21 – 7.16 (m, 4H), 7.13 – 7.05 (m, 5H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.77 (d, *J* = 8.5 Hz, 2H), 6.29 (d, *J* = 15.8 Hz, 1H), 6.17 – 6.09 (m, 1H), 4.71 (t, *J* = 6.6 Hz, 1H), 3.53 (m, *J* = 17.9, 10.5, 5.7 Hz, 2H), 3.03 – 2.87 (m, 1H), 2.78 (dd, *J* = 15.5, 5.4 Hz, 2H), 2.56 (dt, *J* = 14.3, 7.3 Hz, 1H), 2.18 (s, 3H).





Yield: 74%, light yellow oil; ¹H NMR (600 MHz, CDCl₃): δ 7.11 – 7.01 (m, 4H), 6.86 (t, J = 8.7 Hz, 2H), 6.74 (dd, J = 9.0, 4.3 Hz, 2H), 5.38 – 5.31 (m, 2H), 4.51 (t, J = 6.6 Hz, 1H), 3.58 – 3.38 (m, 2H), 2.99 – 2.85 (m, 1H), 2.77 (dt, J = 15.9, 5.0 Hz, 1H), 2.60 – 2.51 (m, 1H), 2.36 (m, J = 16.9, 13.5, 6.2 Hz, 1H), 1.93 – 1.76 (m, 2H), 1.31 – 1.17 (m, 2H), 0.84 – 0.72 (m, 3H). ¹³C

NMR (150 MHz, CDCl₃): δ 155.52, 153.95, 145.38, 137.19, 133.70, 132.03, 130.83, 127.50, 126.39, 125.94, 125.43, 124.63, 114.52, 114.38, 59.40, 41.49, 38.55, 33.69, 26.33, 21.50, 12.66.





Yield: 66%, yellow oil; ¹H NMR (600 MHz, CDCl₃): δ 7.14 – 6.98 (m, 6H), 6.70 (d, J = 8.7 Hz, 2H), 5.33 (tt, J = 15.5, 7.8 Hz, 2H), 4.55 (t, J = 6.7 Hz, 1H), 3.49 (m, J = 17.8, 11.8, 5.3 Hz, 2H), 2.97 – 2.88 (m, 1H), 2.88 – 2.78 (m, 1H), 2.61 – 2.51 (m, 1H), 2.46 – 2.28 (m, 1H), 1.92 – 1.75 (m, 2H), 1.29 – 1.18 (m, 2H), 0.83 – 0.73 (m, 3H). ¹³C NMR (150 MHz, CDCl₃): δ

147.04, 136.98, 133.69, 132.32, 131.14, 127.91, 127.38, 126.37, 125.59, 124.73, 113.72, 58.86, 41.13, 38.60, 33.68, 26.48, 21.47, 12.66.





Yield: 71%, light yellow oil; ¹H NMR (600 MHz, CDCl₃): δ 7.04 (m, J = 12.4, 7.5, 2.9 Hz, 4H), 6.97 (d, J = 8.3 Hz, 2H), 6.74 (t, J = 7.2 Hz, 2H), 5.40 – 5.30 (m, 2H), 4.56 (t, J = 6.5 Hz, 1H), 3.58 – 3.43 (m, 2H), 2.93 (m, J = 14.1, 8.3, 5.4 Hz, 1H), 2.77 (m, J = 15.8, 10.5, 5.2 Hz, 1H), 2.57 (dt, J = 12.5, 7.3 Hz, 1H), 2.45 – 2.28 (m, 1H), 2.17 (s, 3H), 1.92 – 1.76 (m, 2H),

1.29 – 1.18 (m, 2H), 0.82 – 0.75 (m, 3H). ¹³C NMR (150 MHz, CDCl₃): δ 146.52, 137.44, 133.94, 131.84, 130.69, 128.66, 127.42, 126.43, 126.14, 125.29, 124.49, 113.34, 58.99, 41.04, 38.57, 33.71, 26.43, 21.53, 19.23, 12.68.





Yield: 77%,³ colorless oil; ¹H NMR (600 MHz, CDCl₃): δ 7.07 (m, J = 12.2, 8.4, 4.5 Hz, 4H), 6.86 (t, J = 8.6 Hz, 2H), 6.76 (s, 2H), 5.76 (dq, J = 9.8, 7.2 Hz, 1H), 5.03 – 4.92 (m, 2H), 4.56 (t, J = 6.7 Hz, 1H), 3.58 – 3.42 (m, 2H), 2.98 – 2.85 (m, 1H), 2.76 (d, J = 15.9 Hz, 1H), 2.67 – 2.56 (m, 1H), 2.41 (dt, J = 13.9, 6.8 Hz, 1H).





Yield: 70%,³ light yellow oil; ¹H NMR (600 MHz, CDCl₃): δ 7.14 – 7.00 (m, 6H), 6.72 (d, J = 8.9 Hz, 2H), 5.74 (m, J = 17.2, 10.1, 7.2 Hz, 1H), 4.98 (dd, J = 13.5, 6.0 Hz, 2H), 4.60 (t, J = 6.8 Hz, 1H), 3.57 – 3.42 (m, 2H), 2.97 – 2.89 (m, 1H), 2.80 (dt, J = 15.9, 5.4 Hz, 1H), 2.62 (dt, J = 13.9, 6.8 Hz, 1H), 2.40 (dt, J = 14.3, 7.2 Hz, 1H).





7. Reusability of catalyst

The reusability of Pd&Ir#PVBC(L)@SiO₂ is investigated using the α -allylation of *N*-phenyl-1,2,3,4-tetrahydroisoquinoline by cinnamyl acetate as a model reaction under optimized conditions. After the completion of the reaction, the catalyst is recovered by centrifugation and directly reused for the following cycles. It is found that there is only a slight decrease in yield from 78% to 73% in the eighth cycle (Fig. 5a). From the SEM image (Fig. 5b), the 8th-reused Pd&Ir#PVBC(L)@SiO₂ maintains its original well-shaped morphology. Additionally, ICP-OES shows that the contents of anchored Pd/Ir in the 8th-reused catalyst are determined to be 2.07 mmol g⁻¹ and 0.85 mmol g⁻¹, respectively, which indicates that Pd(PPh₃)₄ and Ir(ppy)₂(dtbbpy)PF₆ are partially dissociated. Then the loss of Pd/Ir complexes is responsible for the slight decrease in yields. Based on the above-mentioned catalytic results in efficient synergistic photocatalysis and good reusability of anchored Pd/Ir complexes, it is considered that SiO₂-grafted flexible PVBC brushes is an effective platform for achieving the efficient synergistic photocatalysis of dual Ir/Pd complexes in economical and green manner.



Fig.S19 (a) Yields of the product in the α -allylation of *N*-phenyl-1,2,3,4-tetrahydroisoquinoline by cinnamyl acetate catalysed by Pd&Ir#PVBC(L)@SiO₂. (b) SEM image of 8th-reused Pd&Ir#PVBC(L)@SiO₂.

8. References

- Z. P. Li and C. J. Li, CuBr-catalyzed direct indolation of tetrahydroisoquinolines via cross-dehydrogenative coupling between sp³ C–H and sp² C–H bonds. *J. Am. Chem. Soc.*, 2005, 127, 6968–6969.
- 2 J. Xuan, T. T. Zeng, Z. J. Feng, Q. H. Deng, J. R. Chen, L. Q. Lu, W. J. Xiao and H. Alper, Redox-neutral α-allylation of amines by combining palladium catalysis and visible-light photoredox catalysis, *Angew. Chem. Int. Ed.*, 2015, **54**, 1625–1628.
- 3 P. Wang, K. Meng, S. H. Guo, M. Y. Wang, Y. R. Gao and Y. Q. Wang, Photoinduced α-alkylation of tetrahydroisoquinolines with organoboron reagent enabled by organic photocatalyst. *Eur. J. Org. Chem.*, 2023, **26**, e202201157.