Silica- and polymer-supported platinum(II) polypyridyl complexes: synthesis and application in photosensitized oxidation of alkenes†

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Square-planar polypyridine platinum(II) complexes have been introduced into a silica/polymer matrix by covalent ligand modification. The photophysical properties of the supported matrices are well retained as their model complexes, and the quantum yields for singlet oxygen ($^1O_2$) generation are comparable with that of TPP (tetraphenylporphyrin) under similar conditions. A preliminary application in photosensitized oxidation indicates the silica/polymer-supported matrices are promising, which can be reused without loss of reactivity by a simple filtration. Moreover, the polymer-supported matrix exhibits excellent compatibility in various solvents.

Introduction

Molecular oxygen is one of the most important substances on earth and is involved in many chemical, biological and medical processes. The use of molecular oxygen in chemical production is very attractive in realizing economically and environmentally benign processes. However, the reactivity of oxygen toward most organic molecules is inhibited by its spin restriction due to the triplet ground-state of oxygen. In this regard, photosensitized oxidation holds a special promise, where molecular oxygen can be activated by the excited triplet state of the photosensitizer through an energy transfer process that generates highly reactive singlet oxygen ($^1O_2$). It is well known that singlet oxygen is a versatile reagent for oxidation reactions including cycloaddition reactions to afford endoperoxides, and ene reactions to produce allylic hydroperoxides.[1-5]

Platinum(II) polypyridyl complexes are appealing from a photochemical perspective owing to visible light absorption and the population of the triplet state.[6-12] We and others found that platinum(II) complexes are able to react with molecular oxygen to generate $^1O_2$ with a high quantum yield.[13-15] In the course of extending their applications, we demonstrated that upon irradiation of light in the visible region platinum(II) polypyridyl complexes can be used as sensitizers for photooxidation using molecular oxygen.[16-20] To further extend previous work, we expect to immobilize platinum(II) complexes on silica and polymer supporting matrices in order to make the synthesis, purification and recycling of the photosensitized oxidation more straightforward. The covalent attachment of homogeneous catalysts to silica or polymer supports has been studied widely as an attractive strategy for extending the practical advantages of heterogeneous catalysts to homogeneous systems.[21-27] The potential benefits of heterogenization include facilitation of catalyst separation from reaction mixtures and the simplification of methods for sensitizer recycling. In the present work, we report the synthesis of silica- and polystyrene-bound platinum(II) polypyridyl complexes and their application in photosensitized oxidation of alkenes. A preliminary result suggests that photosensitized oxidation can proceed well using silica- or polymer-supported platinum(II) complexes, and the quantum yields for $^1O_2$ generation are comparable with that of TPP (tetraphenylporphyrin) under similar conditions. Moreover, the matrices have a solvent compatibility and only a simple filtration is needed for the recovery of the platinum(II) polypyridyl complexes without the loss of reactivity.

Results and discussion

Preparation and characteristics of silica-supported matrix

Triethoxysilane modified platinum(II) polypyridyl complex **Pt(tpy)S** was synthesized *via* ligand modification, as shown in Scheme 1a. The ancillary ligand *N*-(3-(triethoxysilyl)propyl)-4-ethynylbenzamide was obtained by a peptide linkage between 4-ethynylbenzoic acid and (3-aminopropyl)-triethoxysilane, which was then reacted with 4′-(*p*-methyl-phenyl)-2,2′:6′,2″-terpyridine platium(II) chloride using CuI-catalyzed chloride-to-alkyne metathesis under ultrasonic conditions to afford the target molecule **Pt(tpy)S**.

Corresponding xerogel **Pt(tpy)SG** was made from **Pt(tpy)S** *via* a sol-gel process (Scheme 1b).[28-30] Typically, **Pt(tpy)S** and tetraethyl orthosilicate (TEOS) were mixed together in a controllable initial proportion, and in which acetic acid and water were used to adjust the pH value to 5–6. The mixture was stirred at 40 °C for enough time until there were sol particles formed in the solution. Then the silica species condensed to link together forming three-dimensional networks. Removal of solvent led to the formation of bulky xerogel **Pt(tpy)SG**. After drying under vacuum overnight, the xerogel was ground and rinsed by solvent for further experiments.

Complex **Pt(tpy)S** in acetonitrile solution exhibits intense vibronic-structured absorption bands at 250–350 nm with extinction coefficients (ε) of the order of 10^4 L mol^{-1} cm^{-1}, and a less

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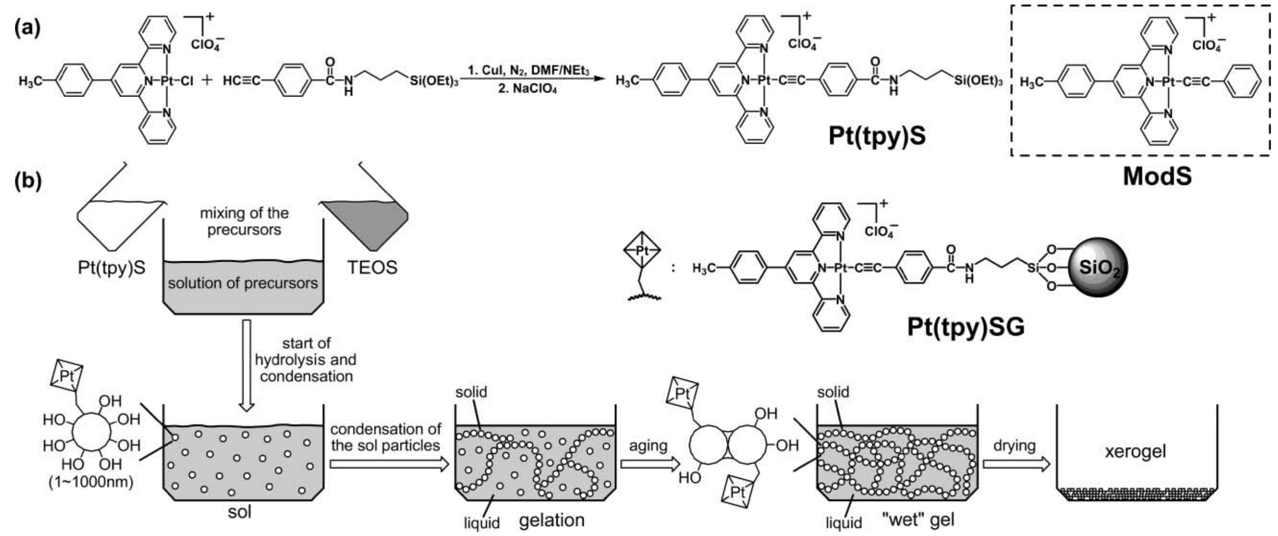


Scheme 1 The preparation of **Pt(tpy)S** and **Pt(tpy)SG**.

intense band at 400–500 nm with ε of the order of 10^3 L mol^{-1} cm^{-1} shown in Table 1. The absorption spectra of **Pt(tpy)S** and the model complex **ModS** were found to follow Beer's Law below the saturated concentration (ESI, Fig. S1†), suggesting no significant complex aggregation occurred. With reference to previous work on platinum(II) terpyridyl complexes,[31] the absorption bands at $\lambda <$ 350 nm are assigned to the intraligand (IL) transition of terpyridyl and acetylide ligand as well as the charge transfer transition involved in the phenylacetylide moiety, while the absorption bands at 425 and 453 nm are ascribed to $d_{yz}(Pt) \rightarrow \pi^*(tpy)$ and $d_{xz}(Pt) \rightarrow \pi^*(tpy)$ MLCT transitions. **Pt(tpy)S** is emissive at 592 nm with a lifetime of 0.71 μs. The correlated luminescence quantum yield (Φ_{em}) of 0.026 were determined by the optical dilute method[32] using a degassed acetonitrile solution of $[Ru(bpy)_3]$-$(PF_6)_2$ as the reference ($\Phi_{em} = 0.062$) (Table 1).[33] The similar photophysical properties of **Pt(tpy)S** and model complex **ModS** indicate that the characteristics of platinum(II) polypyridyl complexes can be well retained with the ancillary ligand modification of triethoxysilane.

The diffusion reflectance UV-visible spectroscopy (UV-DRS) of xerogel **Pt(tpy)SG** displays broad energy absorption bands ranging from 250 to 500 nm, similar to that of **Pt(tpy)S**. The luminescent profile of **Pt(tpy)SG** shows an emission with λ_{max} at 607 nm, and an excitation band at 453 nm (ESI, Fig. S2†). In addition, xerogel **Pt(tpy)SG** is insoluble in normal solvents, thereby leading to convenient separation of silica matrices from reactions.

Preparation and characteristics of polymer-supported matrix

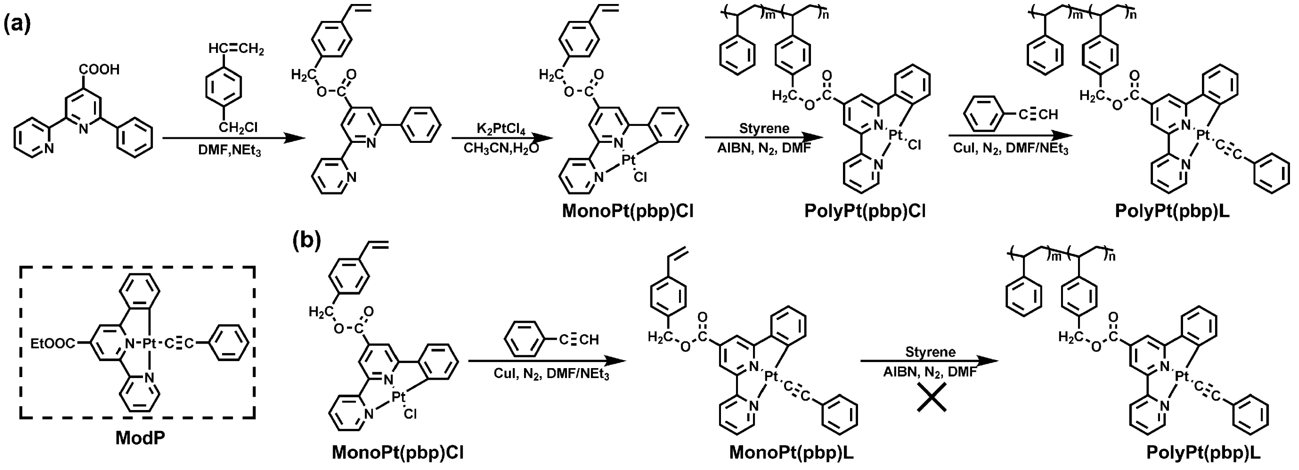
The polymer-supported platinum(II) polypyridyl complex **PolyPt(pbp)L** was prepared by the prepolymerization of **MonoPt(pbp)Cl** and styrene followed by a CuI-catalyzed chloride-to-alkyne metathesis from phenylacetylide ligand to the metal center of platinum(II) (Scheme 2a), which is soluble in various solvents. The ligand of 4-vinylbenzyl 6-phenyl-2,2′-bipyridine-4-carboxylate was synthesized by an ester linkage between 6-penyl-2,2′-bipyridine-4-carboxylic acid and 4-vinylbenzyl chloride, and then it was refluxed with K_2PtCl_4 in a mixture of acetonitrile and water to produce a monomer complex **MonoPt(pbp)Cl**. Initiated by 2,2′-azobisisobutyronitrile (AIBN),[22,34-36] the monomer complex **MonoPt(pbp)Cl** and styrene were polymerized to give the polymer **PolyPt(pbp)L**. It is worth noting that the polymer-supported platinum(II) polypyridyl complex **PolyPt(pbp)L** cannot be prepared by the route shown in Scheme 2b. We originally synthesized the monomer complex **MonoPt(pbp)L** for polymerization. However, the reaction of **MonoPt(pbp)L** and styrene failed to give any desired polymer **PolyPt(pbp)L**, suggesting the monomer complex **MonoPt(pbp)L** may not be stable toward the radical-induced polymerization by AIBN.

The polymer of **PolyPt(pbp)L** exhibits an intense absorption band around 350 nm assignable to the absorption of IL states, and a moderately intense low-energy absorption band in the region of 400–500 nm with two peaks at 459 and 488 nm, respectively,

Table 1 Photophysical characteristics of platinum(II) polypyridyl complexes at room temperature

Entry	λ_{abs}/nm (ε/10^3 L mol^{-1} cm^{-1})	λ_{em}/nm	τ/μs	Φ_{em}
Pt(tpy)S[a]	289 (48.9), 310 (25.9), 337 (19.2), 425 (8.31), 453 (7.18)	592	0.71	0.026
ModS[a]	263 (47.0), 288 (40.2), 313 (24.6), 338 (21.9), 427 (8.17), 454 (7.29)	606	1.03	0.046
Pt(tpy)SG	297, 341, 449[b]	607	—	—
PolyPt(pbp)L[c]	286 (57.4), 348 (21.9), 380 (16.4), 459 (6.64), 488 (6.34)	636	0.25	0.030
ModP[c]	256 (36.6), 283 (42.4), 347 (15.7), 376 (10.8), 458 (5.89), 484 (5.79)	622	0.30	0.030

[a] The solvent is acetonitrile. [b] UV-DRS measurement. [c] The solvent is dichloromethane. The concentration of the polymer **PolyPt(pbp)L** is based on the amount of the functional group.



Scheme 2 The preparation of **PolyPt(pbp)L**.

which are attributed to the absorption of typical MLCT states.[37] The UV/Vis and emission spectra of **PolyPt(pbp)L** in CH_2Cl_2 are also shown in Fig. S3 (ESI†). The correlated maximum emission peak wavelength is at 636 nm, and the luminescence quantum yield is 0.030 and the lifetime is 0.25 μs. As shown in Table 1, **PolyPt(pbp)L** and the model complex **ModP**[38] have similar photophysical characteristics.

Photooxidation

It has been known that the emissive ^{3}MLCT excited states of platinum(II) complexes are responsible for singlet oxygen ($^1O_2$) production.[16,17] To assess the $^1O_2$ generation ability of silica/polymer-supported platinum(II) complexes, 2,2,6,6-tetramethylpiperidine (TMP) was used as a probe to react with $^1O_2$ yielding stable free radical nitroxide (2,2,6,6-tetramethylpiperidine oxide, TMPO), which can be easily detected by electron spin resonance (ESR) spectroscopy.[39,40] The signal of TMPO was clearly monitored when an oxygen saturated solution of TMP and silica/polymer-supported platinum(II) polypyridyl complexes was irradiated by laser beams (ESI, Fig. S4-5†), indicating that $^1O_2$ can be generated efficiently in these systems. The quantum yields for $^1O_2$ generation were determined by the 9,10-diphenylanthrancene bleaching method[41] to be 0.40 for insoluble silica **Pt(tpy)SG** and 0.79 for soluble polymer **PolyPt(pbp)L**;[42] which are comparable to that of TPP (0.56), a well-known photosensitizer under similar conditions.[43]

Several different kinds of olefins were selected to conduct the photosensitized oxidation including three types of singlet oxygen reactions (Table 2).[1] Electron rich stilbene and dimethoxystilbene undergo a [2+2] cycloaddition,[44,45] and the generated endoperoxy intermediates quickly convert to the corresponding phenylaldehyde and methyl benzoate. Cyclopentadiene and 1,3-cyclohexadiene undergo [4+2] cycloaddition with $^1O_2$ to yield endoperoxides, which can be reduced by thiourea to give the corresponding *cis*-cyclodiols,[46] an important chemical for the synthesis of prostaglandins.[47] (1*S*,5*S*)-(−)-α-Pinene can take part in an ene reaction[48,49] to afford hydroperoxy intermediates exclusively. Following reduction by triphenylphosphate, (1*S*,3*S*,5*R*)-(+)-*trans*-3-hydroxypin-2(10)-ene [(+)-*trans*-pinocarveol] can be obtained as a unique product. 7-Dehydrocholesterol is an endogenous compound of the body, involving in a variety of biological processes. Some of its oxidation products possess potent cytotoxic and antitumor activity.[50] The oxidation of 7-dehydrocholesterol is a mixture of [4+2] cycloaddition and ene reaction to produce endoperoxide and hydroperoxides with the molar ratio of 3:1, in line with the reported value of 16:5.[51,52] The mass balance of all the reactions studied in this work were greater than 95%. The yield of photoproducts is based on the consumption of the starting material, and the conversion of the substrates exceeding 90%.

As expected, the recycled use of the sensitizer-supported matrices can be simply achieved by filtration. The polymer **PolyPt(pbp)L** displays an excellent compatibility in various solvents, such as dichloromethane, chloroform, ethyl acetate, DMF and so on. Polar solvents, like methanol, can precipate **PolyPt(pbp)L** for recycling. Dimethoxystilbene was chosen for repeat experiments. The result shows that the silica/polymer-supported matrices are robust enough and do not undergo any degradation after five consecutive runs of the photosensitized reaction.

Conclusions

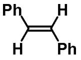
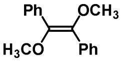
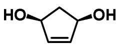
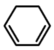
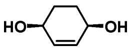
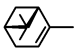
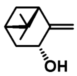
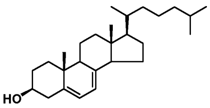
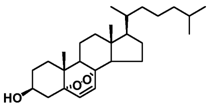
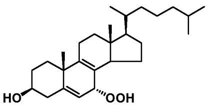
To summarize, we successfully introduced platinum(II) polypyridyl complexes into silica- and polymer matrices by covalent ligand modification. The photophysical properties of the supported matrices are well retained as their model complexes, and the quantum yields for singlet oxygen ($^1O_2$) generation are comparable with that of TPP under similar conditions. A preliminary application to photosensitized oxidation indicates the silica/polymer-supported matrices are promising in all three types of $^1O_2$ reactions, only a simple filtration is needed for the recovery of the platinum(II) polypyridyl complexes without loss of reactivity. Moreover, polymer-supported matrices exhibit excellent compatibility in various solvents and can be precipitated from the reaction by adding polar solvents like methanol.

Experimental

Materials and instrumentation

6-Phenyl-2,2′-bipyridine-4-carboxylic acid, 4′-(*p*-methylphenyl)-2,2′:6′,2″-terpyridine platium(II) chloride and **ModS** were

Table 2 Photosensitized oxidation of alkenes by 0.6 mol% **Pt(tpy)SG** and 2 mol% **PolyPt(pbp)L** in dichloromethane at room temperature

			Yield (%)[a]	
Substrate	Product	Irradiation time (h)	Pt(tpy)SG	PolyPt(pbp)L
	PhCHO	2	~100[b]	~100[b]
	$PhCOOCH_3$	2	~100[c]	~100[c]
		3	>95[d,e]	>95[d,e]
		3	>95[e]	>95[e]
		4	~100[f]	~100[f]
	 , 	3	75, 25	76, 24

[a] Yields were calculated based on the consumption of the substrates. Concentration of the substrates was 5.0×10^{-3} mol L^{-1}. The catalysts' ratio was based on the amount of functional group. [b] Trace amount of *cis*-stilbene was also detected. [c] Trace amount of *cis*-DMOS was also detected. [d] Isolated yield. [e] The products were obtained by reduction using thiourea. [f] The products were obtained by reduction using PPh_3.

synthesized according to the literature methods.[31,37,38] Other reagents were purchased from commercial sources.

UV/vis spectra were measured by a Shimadzu UV-1601PC Spectrophotometer. Fluorescence spectra were run on a Hitachi F-4500. Luminescent decay profiles were obtained by Edinburgh LP 920 using the third harmonic (355 nm) of a pulse Nd:YAG laser as excitation source. The characteristics of the polymer were determined by Waters 515 GPC with columns HP2 & HP3 & HP4 (515 HPLC pump, 2410 RI detector). A gas chromatograph (GC) was monitored on a Shimadzu GC-14B. ESR spectroscopic experiments were carried out at room temperature (298 K) with a Bruker ESP 300E spectrometer.

4-Ethynylbenzoic acid

Ethyl 4-iodobenzoate (3.40 ml, 20.0 mmol), $Pd(PPh_3)_2Cl_2$ (50.0 mg, 0.071 mmol), CuI (75.7 mg, 0.40 mmol) and PPh_3 (65.4 mg, 0.25 mmol) were dissolved in 60 ml solvent of triethylamine and pyridine (1: 1), after degassing, 2-methylbut-3-yn-2-ol (3.90 ml, 40 mmol) was added and the mixture was stirred at room temperature for 2 h. The reaction was quenched by the addition of adequate hydrochloric acid and extracted with dichloromethane; the organic layer was washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by silica gel column chromatography (petroleum ether:ethyl acetate = 6:1), which furnished ethyl 4-(3-hydroxy-3-methylbut-1-ynyl)benzoate (4.0 g, 87% yield) as yellow acicular crystals.

NaH (50%, 1.5 g, 31 mmol) was added to a stirred solution of ethyl 4-(3-hydroxy-3-methylbut-1-ynyl)benzoate (4.0 g, 17.3 mmol) in 200 ml benzene at 75 °C for 1 h, the mixture was distilled slowly until about 50 ml liquid was remaining, the residue was filtered, washed with ethyl acetate, dried over $MgSO_4$, and concentrated. Silica gel column chromatography (petroleum ether:ethyl acetate = 6:1) gave ethyl 4-ethynylbenzoate (1.5 g, 50% yield) as yellow acicular crystals.

Ethyl 4-ethynylbenzoate (1.5 g, 8.6 mmol) was refluxed with NaOH (0.4 g, 10 mmol) in a mixture of methanol and water (30 ml, 1: 5) for 6 h; after the system was cooled down, adequate hydrochloric acid was added until there was a white precipitate formed, filtered solid was recrystallized by methanol, 4-ethynylbenzoic acid (1.1 g, 7.8 mmol, 90% yield) was obtained as white schistous crystals. MS: $m/z = 146$ (M^+). ^1H NMR ($CDCl_3$, 300 MHz) δ: 8.06 (d, $J = 8$ Hz, 2H), 7.59 (d, $J = 8$ Hz, 2H), 3.27 (s, 1H); (CD_3CN, 300 MHz) δ: 8.10 (d, $J = 8$ Hz, 2H), 7.59 (d, $J = 8$ Hz, 2H), 3.91 (s, 1H), 3.53 (b, 1H).

N-(3-(triethoxysilyl)propyl)-4-ethynylbenzamide

4-Ethynylbenzoic acid (300 mg, 2.0 mmol) and $SOCl_2$ (5 ml) were refluxed in THF (20 ml) for 3 h, then the mixture was vacuum distilled to eliminate solvent and excessive $SOCl_2$. The residue was dissolved into 20 ml anhydrous CH_2Cl_2, then another 20 ml CH_2Cl_2 solution of (3-aminopropyl)triethoxysilane (0.60 ml, 2.6 mmol) and 2 ml NEt_3 was dropped in, with the reaction process, there was white precipitate in the system. After filtration, the residue was purified by silica gel column chromatography (petroleum ether:ethyl acetate = 6:1), which furnished *N*-(3-(triethoxysilyl)propyl)-4-ethynylbenzamide (420 mg, 1.2 mmol, 58% yield) as white acicular crystals. MS: $m/z = 349$ (M^+). ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.72 (d, $J = 8$ Hz, 2H), 7.53 (d, $J = 8$ Hz, 2H), 6.53 (b, 1H), 3.83 (q, $J = 8$ Hz, 6H), 3.46 (m, 2H), 3.18 (s, 1H), 1.76 (m, 2H), 1.24 (t, $J = 8$ Hz, 9H), 0.69 (t, $J = 8$ Hz, 2H).

Pt(tpy)S

The mixture of 4′-(*p*-methylphenyl)-2,2′:6′,2″-terpyridine platium(II) chloride (58 mg, 0.098 mmol), *N*-(3-(triethoxysilyl)-propyl)-4-ethynylbenzamide (44 mg, 0.125 mmol), 3 ml DMF and 6 ml NEt_3 was degassed under nitrogen for 15 min, after 6 mg CuI was added, the system was ultrasonicated for 8 h, then 0.5 g $NaClO_4$ was added, the system was ultrasonicated for another hour. The reaction was stopped by the addition of excessive ether, the formed precipitate was filtered, then rinsed by water and ether, the residue was redissolved in acetonitrile, adequate ether was added, the reformed precipitate was filtered and dried, a red solid was obtained (77 mg, 0.080 mmol, 81% yield). HRMS: calcd. for $[C_{40}H_{43}N_4O_4Pt^{194}Si]^+$ 865.2680, found 865.2669 (M^+) (67%); calcd. for $[C_{40}H_{43}N_4O_4Pt^{195}Si]^+$ 866.2701, found 866.2678 (M^+) (100%); calcd. for $[C_{40}H_{43}N_4O_4Pt^{196}Si]^+$ 867.2703, found 867.2698 (M^+) (99%). ^{1}HNMR (DMSO-d_6, 400 MHz) δ: 8.96 (d, J = 8 Hz, 2H), 8.89 (s, 2H), 8.72 (d, J = 8 Hz, 2H), 8.42 (m, 2H), 8.00 (d, J = 8 Hz, 2H), 7.78 (m, 4H), 7.41 (m, 4H), 3.73 (q, J = 7 Hz, 6H), 3.23 (t, J = 7 Hz, 2H), 2.45 (s, 3H), 1.57 (m, 2H), 1.12 (t, J = 8 Hz, 9H), 0.58 (t, J = 8 Hz, 2H). Anal. calcd. for $C_{40}H_{43}ClN_4O_8PtSi\cdot H_2O$: C, 48.80; H, 4.61; N, 5.69. Found: C, 48.12; H, 4.24; N, 5.53.

Pt(tpy)SG

Pt(tpy)S (1.35 mg, 1.40 µmol), TEOS (7.52 g, 36.1 mmol) and 3 ml water were dissolved in 200 ml mixture of acetonitrile and acetone (1: 3), 3 ml 36% acetic acid was added to the system to adjust the pH to around 5, the mixture was stirred at 40 °C for 24 h, after removal of the solvent the bulk gel was dried under vacuum at 60 °C for 24 h, the solid was ground entirely with a carnelian mortar, the crude product was rinsed with acetonitrile and acetone, a slightly yellow powder **Pt(tpy)SG** (2.30 g) was obtained after further drying under vacuum overnight. With various initial proportions of **Pt(tpy)S** *vs* TEOS, **Pt(tpy)SG** of different loading amounts were obtained for further experiments.

4-Vinylbenzyl 6-phenyl-2,2′-bipyridine-4-carboxylate

The mixture of 6-phenyl-2,2′-bipyridine-4-carboxylic acid (510 mg, 1.85 mmol), 4-vinylbenzyl chloride (0.50 ml, 3.5 mmol), 3 ml DMF and 6 ml NEt_3 was stirred at room temperature for 24 h. The reaction was quenched by addition of excessive water, the precipitate was filtered and purified by silica gel column chromatography (petroleum ether:ethyl acetate = 6:1), which furnished 4-vinylbenzyl 6-phenyl-2,2′-bipyridine-4-carboxylate (647 mg, 1.65 mmol, 90% yield) as white schistous crystals. MS: m/z = 392(M^+). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 5.28 (d, J = 11 Hz, 1H), 5.46 (s, 2H), 5.80 (d, J = 17 Hz, 1H), 6.76 (dd, J = 18 and 11 Hz, 1H), 7.51 (m, 8H), 7.96 (m, 1H), 8.20 (d, J = 7 Hz, 2H), 8.39 (s, 1H), 8.66 (d, J = 8 Hz, 1H), 8.80 (d, J = 3 Hz, 1H), 8.99 (s, 1H).

MonoPt(pbp)Cl

The mixture of 4-vinylbenzyl 6-phenyl-2,2′-bipyridine-4-carboxylate (520 mg, 1.32 mmol) and K_2PtCl_4 (550 mg, 1.32 mmol) was refluxed in a mixture of acetonitrile and water (150 ml, 1: 1) for 48 h. The precipitate was filtered and rinsed with a mixture of acetonitrile and water, which furnished **MonoPt(pbp)Cl** (733 mg, 1.18 mmol, 90% yield) as a red solid. FAB-MS: m/z = 621 (M^+). ^{1}HNMR (DMSO-d_6, 400 MHz) δ: 5.42 (d, J = 11 Hz, 1H), 5.59 (s, 2H), 6.00 (d, J = 18 Hz, 1H), 6.90 (dd, J = 18 and 12 Hz, 1H), 7.17 (t, J = 7 Hz, 1H), 7.25 (t, J = 7 Hz, 1H), 7.56 (d, J = 7 Hz, 1H), 7.69 (m, 4H), 7.73 (d, J = 7 Hz, 1H), 8.03 (t, J = 7 Hz, 1H), 8.23 (s, 1H), 8.44 (t, J = 7 Hz, 1H), 8.51 (s, 1H), 8.75 (d, J = 8 Hz, 1H), 8.92 (d, J = 8 Hz, 1H). Anal. Calcd. for $C_{26}H_{19}ClN_2O_2Pt$: C, 50.21; H, 3.08; N, 4.50. Found: C, 50.07; H, 3.24; N, 4.15.

MonoPt(pbp)L

The mixture of **MonoPt(pbp)Cl** (125 mg, 0.020 mmol, according to the amount of the functional group Pt(bpy)Cl), phenyl acetylene (4.0 µl, 0.036 mmol), 5 ml DMF and 10 ml NEt_3 was degassed under nitrogen for 15 min, after 6 mg CuI was added, the system was kept in ultrasonic conditions for 8 h. The reaction was quenched by the addition of adequate ether after the system cooled down. The formed precipitate was filtered and rinsed by water and ether, then redissolved in dichloromethane; after filtering, the solution was concentrated to a suitable small volume, excessive ether was added, the reformed precipitate was filtered and rinsed by ether again, which furnished a salmon solid **MonoPt(pbp)L** (112 mg, 82% yield). FAB-MS: m/z = 687 (M^+). ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 5.42 (d, J = 11 Hz, 1H), 5.59 (s, 2H), 6.00 (d, J = 18 Hz, 1H), 6.90 (dd, J = 18 and 12 Hz, 1H), 7.18 (t, J = 7 Hz, 1H), 7.25 (t, J = 7 Hz, 1H), 7.33–7.51 (m, 4H), 7.68–7.79 (m, 7H), 7.97 (m, 1H), 8.31 (m, 1H), 8.42 (m, 1H), 8.59 (m, 1H), 8.73 (d, J = 8 Hz, 1H), 9.04 (d, J = 8 Hz, 1H). Anal. Cacld. for $C_{34}H_{24}N_2O_2Pt$: C, 59.39; H, 3.52; N, 4.07. Found: C, 59.27; H, 3.36; N, 3.88.

PolyPt(pbp)Cl

MonoPt(pbp)Cl (108 mg, 0.173 mmol) and styrene (2.00 ml, 17.3 mmol) was dissolved in 30 ml anhydrous DMF, after degassing for 15 min, AIBN (2,2′-azobisisobutyronitrile, 48 mg, 0.29 mmol) was added and the mixture was stirred at 75 °C for 24 h. The reaction was quenched by the addition of adequate methanol after the system cooled down. The formed precipitate was filtered and rinsed by methanol, then redissolved in dichloromethane, excessive methanol was added, the reformed precipitate was filtered and rinsed by methanol again, which furnished **PolyPt(pbp)Cl** (1.74 g, 90% yield) as a red solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.40 (br, 2H), 1.85 (br, 1H), 6.65 (br, 2H), 7.05 (br, 3H), 8.60 (br, minor). The characteristics of the polymer were determined by gel permeation chromatography (GPC) calibrated with polystyrene standards in THF. M_n: 5037, M_w: 14714, PDI: 2.92.

PolyPt(pbp)L

The mixture of **PolyPt(pbp)Cl** (355 mg, 0.032 mmol, according to the amount of functional group Pt(bpy)Cl), phenylacetylene (4.0 µl, 0.036 mmol), 6 ml DMF and 10 ml NEt_3 was degassed under nitrogen for 15 min; the system was ultrasonicated for 8 h after 10 mg CuI was added. The reaction was quenched by the addition of adequate methanol after the system had cooled down. The formed precipitate was filtered and rinsed by methanol, then redissolved in dichloromethane, excessive methanol was added, the reformed precipitate was filtered and rinsed by methanol again, which furnished a salmon solid **PolyPt(pbp)L** (287 mg, 80% yield). ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 1.40 (br, 2H), 1.80 (br, 1H), 6.70 (br, 2H), 7.10 (br, 3H), 8.70 (br, minor). The characteristics of the polymer were determined by gel permeation chromatography calibrated with polystyrene standards in THF. M_n: 6720, M_w: 16370, PDI: 2.43.

Photooxidation experiments

The sample in a Pyrex® reactor was bubbled with oxygen during irradiation. A 500 W high-pressure Hanovia Hg lamp was employed as the light source; a quartz jacket with water circulation was used to cool the lamp. A glass filter was used to cut off light with a wavelength below 400 nm and guaranteed irradiation with visible light. The products were monitored by GC, GC-MS and ^{1}H-NMR.

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