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Development of dipyridine-based coordinative polymers for reusable heterogeneous catalysts

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Abstract

Poly(di(pyridin-2-yl)methyl acrylate) (PDPyMA), which was obtained by the free radical polymerization of designed coordinative monomer of di(pyridin-2-vl) methyl acrylate, is able to coordinate with various metal ions to form heterogeneous catalysts for diverse catalytic reactions. The Pd and Cu complexes supported by PDPyMA were developed for the heterogeneous Suzuki-Miyaura reaction and Friedel-Crafts alkylation, respectively. The PDPyMA-based catalysts showed no significant decline of reactivity after five times recycling. However, the hydrolysis of the PDPyMA backbone under alkaline conditions limited the catalytic efficiency of this heterogeneous catalyst so that the coordinative monomer was redesigned as 1,1-di(pyridine-2-yl)-2-(4-vinylphenyl)ethan-1-ol and then 2,2'-(1-methoxy-2-(4-vinylphenyl)ethane-1,1-diyl)dipyridine (MVPhDPy). With copolymerization of N-isopropyl acrylamide (NIPAM), the efficiency of polymer-based heterogeneous catalysts could be further raised, demonstrated by the increased turn over number in the Suzuki-Miyaura reaction, which approached 5,260 by using the catalyst formed from poly(MVPhDPy-co-NIPAM) and Pd(OAc)₂. poly(MVPhDPy-co-NIPAM) copolymer, therefore, could be a versatile platform to support different metal ions for various heterogeneous catalytic reactions.

KEYWORDS

coordinative polymer, heterogeneous catalyst, reusable catalyst

1 | INTRODUCTION

Development of reusable heterogeneous catalysts is one of the most important subjects in organic synthesis and organometallic catalysis due to the economic and environmental concerns.^[1-12] Different substrates such as porous materials or particles,^[13,14] metal-organic-frameworks,^[15,16] and crosslinked polymers^[17–21] have been used to carry metal ions or particles as solid catalysts for the mediation of various reactions. However, compared with homogeneous

systems, there are still some challenges such as low catalytic efficiency and gradually declined activity after reuse.[22-24] The coordinating site of the substrates is another issue that limits the application of these heterogeneous catalysts because many valuable reactions can only be mediated by the organometallic complexes with unique ligands. Herein, a series of coordinative monomers were designed for the polymeric backbone that can bind to the metal ions (Scheme 1). The polymeric palladium and copper complexes coordinated by poly(di(pyridin-2-yl)methyl acrylate) (PDPyMA) were

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capable of catalyzing the Suzuki-Miyaura reaction and Friedel-Crafts alkylation, respectively, without significant decline in reactivity after five times recycling. 1,1-di(pyridine-2-yl)-2-(4-vinylphenyl)ethan-1-ol (DPyVPhE) was then synthesized to avoid the hydrolysis of ester bond in di(pyridin-2-yl)methyl acrylate (DPyMA) and thus increased the turn over number (TON) in the Suzuki-Miyaura reaction from 26 to 62. The TON in the Suzuki-Miyaura reaction catalyzed by the polymeric palladium complex could be further improved to 136 by using the copolymer of DPyVPhE and *N*-isopropyl acrylamide (NIPAM) as the polymer backbone. 2,2'-(1-methoxy-2-(4-vinylphenyl)ethane-1,1-diyl)dipyridine (MVPhDPy), which was obtained from the methylation of DPyVPhE, showed a higher stability under various reaction



Poly(MVPhDPy-co-NIPAM)-Pd(OAc)₂ Poly(DPyVPhE-co-NIPAM)-Pd(OAc)₂ Suzuki-Miyaura TON = 5260, TOF = 263 Suzuki-Miyaura TON = 136, TOF = 34

SCHEME 1 The evolution of heterogeneous catalysts based on coordinative polymers in this study

conditions and thus the heterogeneous catalyst based on the copolymer of MVPhDPy and NIPAM could catalyze the Suzuki-Miyaura reaction without a significant decrease in activity after five times recycling and approached the TON of 5,260. These coordinative polymers could be a versatile platform to carry different metal ions for the heterogeneous catalysis of varied reactions.

2 | **RESULTS AND DISCUSSION**

2.1 | Synthesis and characterization of DPyMA, PDPyMA, and their metal complexes

The synthetic steps of PDPyMA-based heterogeneous catalysts are shown in Scheme 2. The di(pyridin-2-yl)methyl acrylate^[25] was obtained as a yellowish liquid from the acetvlation of dipyridinyl methanol, which was prepared from a halogen-metal exchange of 2-bromopyridine and *n*-butyllithium followed by nucleophilic addition to the aldehvde. Crystal structure of the complex of DPvMA and CuBr₂ indicated that DPyMA could coordinate to the metal ion by pyridinyl groups with the formula of [(DPyMA)CuBr $(\mu$ -Br)]₂ (Figure 1), in which the copper atoms locate in a square pyramidal environment. The nitrogen atoms of pyridinyl groups are at the square base and coordinate to copper centers with an average Cu-N bond length equal to 2.03 Å.^[26] The DPvMA and copper formed a sixmembered ring with the boat conformation. The bromides at square base coordinate to the copper center as a regular Cu(II)-Br bond with bond lengths around 2.41 Å.^[26,27] However, the bridged bromides at the apex position show a bond length larger than 3.00 Å, indicating a weak coordination. Free radical polymerization of DPyMA initiated by azobisisobutyronitrile (AIBN) in Dimethylformamide (DMF) at 60°C gave PDPyMA, which was characterized by gel permeation chromatography (GPC) and the ¹H NMR spectrum (Figure 2). A representative PDPyMA product was a yellow powder with molecular weight equal to



SCHEME 2 Synthetic steps of DPyMA, poly(di(pyridin-2-yl)methyl acrylate) (PDPyMA), and their metal complexes

23,400 g/mol and D value equal to 1.80 (Figure 2b). The reaction of PDPyMA and metal salts in dichloromethane at room temperature provided insoluble powders that could hardly be dissolved in CH₂Cl₂, EtOAc, MeOH, and H₂O (Figure S5–S6). According to the single-crystal structure of [(DPyMA)CuBr(μ -Br)]₂, the insolubility could be attributed



FIGURE 1 Crystal structure of [(DPyMA)CuBr(µ-Br)]₂ depicted with ellipsoids at the 50% probability. Selected bond lengths (Å) and angles (°) for [(DPyMA)CuBr(µ-Br)]₂: Cu(1)-N(1) 2.031(5), Cu(1)-N (2) 2.037(5), Cu(1)-Br(2) 2.3936(10), Cu(1)-Br(1) 2.4306(9), Cu(1)-Br (3) 3.0736(12), Cu(2)-N(3) 2.023(5), Cu(2)-N(4) 2.058(5), Cu(2)-Br (3) 2.4128(9), Cu(2)-Br(4) 2.4360(10), Cu(2)-Br(1) 3.0152(12), C(13)-C(14) 1.329(10), C(27)-C(28) 1.327(10), N(1)-Cu(1)-N(2) 86.0(2), N (1)-Cu(1)-Br(2) 89.67(15), N(2)-Cu(1)-Br(2) 160.97(16), N(1)-Cu(1)-Br(1) 175.68(17), N(2)-Cu(1)-Br(1) 93.05(14), Br(2)-Cu(1)-Br (1) 92.59(3), N(1)-Cu(1)-Br(3) 90.18(16), N(2)-Cu(1)-Br(3) 91.36(16), Br(2)-Cu(1)-Br(3) 107.18(4), Br(1)-Cu(1)-Br(3) 85.64(3), N(3)-Cu(2)-N(4) 85.3(2), N(3)-Cu(2)-Br(3) 175.41(15), N(4)-Cu(2)-Br(3) 90.33 (14), N(3)-Cu(2)-Br(4) 88.12(15), N(4)-Cu(2)-Br(4) 161.23(17), Br(3)-Cu(2)-Br(4) 95.63(3), N(3)-Cu(2)-Br(1) 94.69(16), N(4)-Cu(2)-Br (1) 98.07(16), Br(3)-Cu(2)-Br(1) 87.27(3), Br(4)-Cu(2)-Br(1) 99.97(3), Cu(1)-Br(1)-Cu(2) 94.09(3), and Cu(2)-Br(3)-Cu(1) 93.00(3)

to the combination of polar metal center and nonpolar polymer chain or the formation of a polymer network architecture cross-linked via metal ions. The yellow powder formed from PDPyMA and Pd(OAc)₂ with 138.8 ppm of Pd²⁺ (Catalyst 1a), and the pale blue powder formed from PDPyMA and Cu(OTf)₂ with 76.7 ppm of Cu²⁺ (Catalyst 1b) were used as the heterogeneous catalysts for the Suzuki-Miyaura reaction and Friedel-Crafts alkylation, respectively.

2.2 | Suzuki-Miyaura reaction catalyzed by PDPyMA-Pd(OAc)₂

Suzuki-Mivaura reaction^[28-32] is one of the most versatile and well-developed methods in organic synthesis for carbon-carbon bond formation using palladium complexes and thus was selected to evaluate the performance of heterogeneous catalyst of PDPyMA-Pd(OAc)₂ (Table 1). The coupling reaction of 4-tolyboronic acid and bromobenzene in *o*-xylene at $90^{\circ}C^{[33,34]}$ was applied to optimize the catalyst loading. The yield reached 70% within 4 hr when 0.02 g of PDPyMA-Pd(OAc)₂ was used in the reaction and could be improved to 94% by increasing the loading of Catalyst 1a to 0.10 g (Table 1, Entries 1 and 2). The reuse of Catalyst 1a for another four times showed almost no difference in the yield and the palladium leakage in the solution detected by inductively coupled plasma atomic emission spectroscopy (ICP-AES) was around 0.004 mg in average, which was equal to 0.029%. The same reaction was also catalyzed by the monomeric complex of DPyMA-Pd(OAc)₂ to give a 99% yield with a lower TON (Table 1, Entry 3), which implied that the polymeric structure and heterogeneity of PDPyMA-Pd(OAc)₂ did not damage the activity of individual palladium center. The electron-withdrawing group such as -NO₂ on the reactant was expected to promote the reaction to a higher yield and thus a better TON number.^[35-38] Indeed, the yield of the Suzuki-Miyaura reaction catalyzed by PDPyMA-Pd(OAc)₂ approached 99% within 4 hr with a



FIGURE 2 (a) ¹H NMR (CDCl₃, 400 MHz) spectrum and (b) GPC trace of the representative poly(di(pyridin-2-yl) methyl acrylate). $M_n = 23,400$ g/mol and D = 1.80



R = -H, Yield, Pd leakage^b: first cycle: 99%, 0.014%. Fourth cycle: 99%, 0.014%Second cycle: 99%, 0.058%. fifth cycle: 92%, 0.029%Third cycle: 99%, 0.029% $<math display="block">R = -NO_2, Yield, Pd leakage: first cycle: 99\%, 0.036\%. Fourth cycle: 99\%, 0.036\%$ Second cycle: 99%, 0.036%. Fifth cycle: 92%, 0.05%Third cycle: 99%, 0.043%<math display="block">R = -OMe, Yield, Pd leakage: first cycle: 70%, 0.086%. Fourth cycle: 75%, 0.086%Second cycle: 70%, 0.065%. Fifth cycle: 68%, 0.094%

Third cycle: 65%, 0.086%

Entry	R	Loading (g) ^c	Yield (%) ^d	TON ^e	$TOF(h^{-1})$
1	Н	0.02	70	26	6.5
2	Н	0.1	94	7.3	1.8
3^{f}	Н	0.1	99	4.6	1.2
4	NO_2	0.1	99	7.6	1.9
5	OMe	0.1	70	5.3	1.3

^aConditions: R-bromobenzene (1.00 mmol), 4-tolyboronic acid (1.5 mmol), PDPyMA-Pd(OAc)₂ (0.10 g,

13.88 mg Pd on the polymer), K_2CO_3 (0.28 g, 1.95 mmol), o-xylene (2 mL), 90°C, 4 hr.

^bMetal leakage was determined by ICP-AES.

^cThe quantity of the catalyst.

^dThe yield was calculated by the ¹H NMR spectrum with the internal standard of mesitylene.

^eTurnover number (TON) was determined from the quantity of product and catalyst.

^fUsing DPyMA-Pd(OAc)₂ as a catalyst.

TON equal to 7.6 when 1-bromo-4-nitrobenzene was used as the reactant (Table 1, Entry 4). The activity of Catalyst 1a showed no observable difference after five times recycling with an average loss of palladium as 0.009 mg (0.065%). On the other hand, when bromobenzene had an electrondonating group like —OMe, the catalytic efficiency in the Suzuki-Miyaura reaction would be decreased as shown by the declined yield of 70% in the coupling reaction of 4-bromoanisole and 4-tolyboronic acid catalyzed by PDPyMA-Pd(OAc)₂ (Table 1, Entry 5).

2.3 | Friedel-Crafts alkylation catalyzed by PDPyMA-Cu(OTf)₂

Friedel-Crafts alkylation is another well-known organic reaction mediated by Lewis acid catalysts for the formation of carbon–carbon bonds.^[39–42] Therefore, the heterogeneous catalyst of PDPyMA-Cu(OTf)₂ was applied to mediate the Friedel-Crafts reaction of indol and methyl 3,3,3trifluoropyruvate in ether at 0°C for 20 hr to demonstrate that PDPyMA could be a platform carrying different metal ions to catalyze the corresponding reactions. The yield was raised from 0 to 80% as the PDPyMA-Cu(OTf)₂ was increased from 0.02 to 0.50 g (Table 2, Entries 1–3). Catalyst 1b was then recycled by filtration and then reused to mediate the reaction for another four times, which showed a constant yield around 80% and the average metal leakage as 0.024 mg that was equal to 0.063% loss of copper species. The reaction catalyzed by the monomeric complex of DPyMA-Cu(OTf)₂, which was performed as a control study, reached 99% yield but showed a lower TON (Table 2, Entry 4), implying that the transformation from homogeneous to heterogeneous catalysis of Friedel-Crafts alkylation using PDPyMA platform does not significantly affect the catalytic activity. These results demonstrated that PDPyMA can be a multifunctional matrix to carry various metal ions for the catalysis of different reactions.

2.4 | Synthesis of DPyVPhE and its palladium complex

A common strategy to improve the catalytic efficiency of a Suzuki-Miyaura reaction was the addition of strong base, which causes the hydrolysis of the ester bond in DPyMA.

TABLE 1 Suzuki-Miyaura reactions

 of different bromo-benzene and

 4-tolyboronic acid mediated by

 Catalyst 1a^a

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TABLE 2 Friedel-Craft alkylation of indole and methyl 3,3,3-trifluoropyruvate mediated by Catalyst 1b^a



Yield, Pd leakage^b: First cycle: 80%, 0.097%. Fourth cycle: 81%, 0.037%

Second cycle: 82%, 0.052%. Fifth cycle: 80%, 0086% Third cycle: 80%, 0.044%

Entry	Loading (g) ^c	Yield (%) ^d	TON ^e	$TOF(h^{-1})$
1	0.02	0	0	0
2	0.30	50	1.4	0.07
3	0.50	80	1.3	0.065
4 ^f	0.50	99	0.7	0.035

^aConditions: Indole (0.55 mmol), methyl 3,3,3-trifluoropyruvate (50 μ L, 0.5 mmol), Et₂O (2 mL), PDPyMA-Cu (OTf)₂ (0.5 g, 38.25 mg Cu on the polymer), 0°C, 20 hr.

^bMetal leakage was determined by ICP-AES.

^cThe quantity of the catalyst.

^dThe yield is calculated by the ¹H NMR spectrum.

eTurnover number (TON) was determined from the quantity of product and catalyst.

 $^{\rm f}$ Using DPyMA-Cu(OTf)₂ as a catalyst.



SCHEME 3 The synthetic process of the coordinative monomers of 1,1-di(pyridine-2-yl)-2-(4-vinylphenyl)Ethan-1-ol and 2,2'-(((4-vinylbenzyl]oxy)methylene)dipyridine (4-VBMDPy)

Therefore, we redesigned the monomer by replacing the ester group using the benzyloxide group and targeted to the new monomer of 2,2'-(((4-vinylbenzyl)oxy)methylene) dipyridine (4-VBMDPy).^[43] However, the reaction of dipyridinyl methanol and 4-vinylbenzyl chloride generated 4-VBMDPy as the minor product but DPyVPhE as the major product (Scheme 3), which was rarely reported. The structure of the major product was further confirmed by X-ray crystallography (Figure 3). The ORTEP diagram clearly showed that the new coordinative monomer has a vinyl group and two pyridines linked by a 2-phenylethan-1-ol segment. To rationalize this unexpected result, a series of reactions using benzyl halide and varied methanol derivatives as the model compounds were performed (Table 3).



FIGURE 3 ORTEP diagram of DPyVPhE depicted with ellipsoids at the 50% probability. Selected bond lengths (Å) and angles (°) for DPyVPhE: O(1)-C(1) 1.411(3), N(1)-C(11) 1.322(5), N(1)-C (15) 1.341(5), N(2)-C(20) 1.333(5), N(2)-C(16) 1.335(4), C(9)-C (10) 1.234(7), C(11)-N(1)-C(15) 118.4(3), C(20)-N(2)-C(16) 117.3(3), O(1)-C(1)-C(16) 109.2(2), O(1)-C(1)-C(11) 108.9(2), O(1)-C(1)-C (2) 108.3(2), N(1)-C(11)-C(12) 122.8(3), N(1)-C(11)-C(1) 114.4(3), N (1)-C(15)-C(14) 123.0(4), N(2)-C(16)-C(17) 122.6(3), N(2)-C(16)-C (1) 115.8(3), and N(2)-C(20)-C(19) 124.1(3)

4-VBMDPy should be synthesized via the O-alkylation pathway and DPyVPhE was obtained via the C-alkylation pathway. Given by the reactions with various methanol derivatives, it was realized that two 2-pyridine groups were required for the generation of DPyVPhE (Table 3, Entries 1–5). When there was only 0.5 equivalent of NaH, the



Entry	R ₁	R ₂	R ₃	Base (equiv.)	Τ (° C)	Conv. Of O-alkylation (%)	Conv. Of C-alkylation (%)
1	2-Pyridine	2-Pyridine	Cl	NaH (1.2)	25	15	77
2	Phenyl	Phenyl	Cl	NaH (1.2)	25	60	_
3	3-Pyridine	3-Pyridine	Cl	NaH (1.2)	25	20	_
4	2-Pyridine	Phenyl	Cl	NaH (1.2)	25	41	_
5	2-Pyridine	Н	Cl	NaH (1.2)	25	42	_
6	2-Pyridine	2-Pyridine	Cl	NaH (0.5)	25	21	18
7	2-Pyridine	2-Pyridine	Cl	NaH (0.9)	25	22	62
8	2-Pyridine	2-Pyridine	Cl	NaH (1.6)	25	10	83
9	2-Pyridine	2-Pyridine	Cl	NaH (2.2)	25	_	92
10	2-Pyridine	2-Pyridine	Br	NaH (1.6)	25	54	32
11	2-Pyridine	2-Pyridine	Ι	NaH (1.6)	25	30	2
12	2-Pyridine	2-Pyridine	Cl	LDA ^a (1.2)	25	_	_
13	2-Pyridine	2-Pyridine	Cl	t-BuOK (1.2)	25	5	47
14	2-Pyridine	2-Pyridine	Cl	TMS ₂ NNa ^b (1.2)	25	5	49
15	2-Pyridine	2-Pyridine	Cl	TEA ^c (1.2)	25	_	_
16	2-Pyridine	2-Pyridine	Cl	NaH (1.2)	-20	_	_
17	2-Pyridine	2-Pyridine	Cl	NaH (1.2)	60	_	78

^aLithium diisopropylamide.

^bSodium bis(trimethylsilyl)amide.

^cTriethylamine.

conversion of O-alkylation and C-alkylation pathways were comparable but the total conversion was low (Table 3, Entry 6). The increase of NaH raised the efficiency of C-alkylation as well as the total conversion (Table 3, Entries 7 and 8). The product of C-alkylation became the only product with 92% conversion when 2.2 equivalent of NaH was added (Table 3, Entry 9). The O-alkylation could dominate the reaction when benzyl bromide or benzyl iodide was used, however, the total conversion decreased (Table 3, Entries 10 and 11). Changing the base only lowered the total conversion but could not reverse the majority from C-alkylation to O-alkylation (Table 3, Entries 12–14). The temperature did not affect the reaction pathway significantly. When the temperature was too low, reaction does not occur (Table 3, Entry 16), but when the temperature increased to 60°C, Calkylation is the only pathway with comparable conversion to that at 25°C (Table 3, Entry 17). Because the organic synthesis and mechanism are not the main concern in this study and the optimized conditions for the generation of 4-VBMDPy may not be achieved within a predictable time period, DPyVPhE, which is also a vinyl monomer that can coordinate to metal ions, was used in the following study.

The complex of DPyVPhE-Pd(OAc)₂ was then synthesized and characterized using X-ray crystallography to recognize the possible coordination of PDPyVPhE to Pd²⁺ ions (Figure 4). DPyVPhE-Pd(OAc)₂ was found to be a triclinic crystal with the *P*-1 space group (Table S1). The palladium center was coordinated by two pyridines of DPyVPhE and two acetate groups to form a square planar configuration. The bond lengths of Pd-N and Pd-O are 2.007 and 2.016 Å, respectively, which matched the range reported in the literature.^[44,45] This square planar N, N, O, O coordinated

SCHEME 4 Synthetic steps of PDPyVPhE-Pd(OAc)₂ (Catalyst 2)

TABLE 4 Suzuki-Miyaura reaction catalyzed by heterogeneous catalyst of PDPyVPhE-Pd(OAc)₂ with different

bases in varied solvents^a





Entry	X	R	Solvent	Base	Yield (%) ^b	TON ^c	$TOF(h^{-1})$
1	Br	Н	o-Xylene	K ₂ CO ₃	78	50	13
2	Br	Н	DMF	K ₂ CO ₃	28	18	5
3 ^d	Br	Н	H_2O	K ₂ CO ₃	76	49	12
4	Br	Н	Toluene	K_2CO_3	64	41	10
5	Br	Н	o-Xylene	KOH	96	62	15
6	Br	OMe	o-Xylene	KOH	89	58	15
7	Br	CN	o-Xylene	KOH	99	64	16
8	Br	NO_2	o-Xylene	KOH	99	64	16
9 ^e	Ι	Н	o-Xylene	KOH	89	116	58

^aConditions: bromobenzene (1 mmol), 4-tolylboronic acid (1.5 mmol), base (0.95 mmol), solvent (2 mL), Catalyst 2 (1.6 mol%), 90°C, 4 hr.

^bThe yield was calculated by the ¹H NMR spectrum with the internal standard of mesitylene.

^cTurnover number (TON) was determined from the quantity of product and catalyst.

^dTBAB (2 mmol).

eCatalyst 2 (0.77 mol%), 2 hr.

configuration of DPyVPhE-Pd $(OAc)_2$ provides a suitable environment for the catalysis of the Suzuki-Miyaura reaction.^[46]

2.5 | Suzuki-Miyaura reaction catalyzed by PDPyVPhE-based palladium complexes

The synthetic steps of PDPyVPhE-Pd(OAc)₂ (Catalyst 2) are similar to that of PDPyMA-Pd(OAc)₂. PDPyVPhE $(M_n = 69,200 \text{ g/mol}, D = 4.3)$, which was obtained from the free radical polymerization of DPyVPhE initiated by AIBN in toluene at 60°C for 48 hr, was reacted with Pd(OAc)₂ in CH₂Cl₂ at 25°C for 2 hr to obtain the orange powder of heterogeneous catalyst of PDPyVPhE-Pd(OAc)₂ (Scheme 4). The palladium content of Catalyst 2 was measured by ICP-AES as 17.0% (wt/wt) (1.70 mg, 2 monomer per Pd, 111 Pd

per polymer chain). This heterogeneous catalyst was then used to mediate the Suzuki-Miyaura reaction of 4-tolyboronic acid and bromobenzene with different bases in varied solvents. The reaction in o-xylene using potassium hydroxide (KOH) as the base demonstrated the highest yield as 96% as well as the highest TON as 63 compared to the values of reactions in DMF, H₂O, and toluene using K₂CO₃ as the base (Table 4, Entries 1–5). The electron-donating substituent on bromobenzene led to a lower catalytic efficiency (Table 4, Entry 6) and reversely, the electronwithdrawing group raised the conversion and TON of the reaction (Table 4, Entries 7 and 8), which matched the trend reported in the literature.^[35–38] The TON could approach a higher value of 116 in the reaction of 4-tolyboronic acid and iodobenzene with a shorter reaction time (Table 4, Entry 9).^[47,48] However, the leakage of Pd species was significant during the recycling process and thus we tried to improve Catalyst 2 by the modification of the polymer backbone.

The addition of NIPAM into the polymer backbone was reported to be able to improve the reactivity of polymerbased heterogeneous catalyst^[49,50] so that free radical copolymerization of DPyVPhE and NIPAM was performed under the condition of (AIBN)₀/(DPyVPhE)₀/(NIPAM)₀ = 1/3.3/6.7 in toluene at 60°C for 48 hr (Scheme 5). The copolymer ($M_n = 86,300$ g/mol, D = 1.6), which was characterized by GPC and ¹H NMR to confirm the coexistence of DPyVPhE and NIPAM (Figure S3), was then mixed with Pd(OAc)₂ to form a new DPyVPhE-based heterogeneous catalyst (Catalyst 3). The palladium content of Catalyst 3 was also measured using ICP-AES as 8.1% (0.81 mg, DPyVPhE/Pd = 1.4, 66 Pd per polymer chain). Compared to Catalyst 2, the palladium content was decreased but the DPyVPhE/Pd ratio was increased, which was a more economical way for the utilization of coordinative monomer.

The condition of the Suzuki-Miyaura reaction of 4-tolyboronic acid and bromobenzene catalyzed by Catalyst 3 was also optimized by verifying the solvent and base (Table 5, Entries 1–7). Similar to Catalyst 2, Catalyst 3 showed the highest catalytic activity as the TON equal to 136 when the reaction was performed using KOH as a base



SCHEME 5 Synthetic steps of poly(DPyVPhE-*co*-NIPAM)-Pd(OAc)₂ (Catalyst 3)

TABLE 5 Suzuki-Miyaura reaction catalyzed by Catalyst 3 with varied solvents and bases^a

B(OH)₂ + R Catalyst 3 solvent, base, 90 °C, Time

R = -H, X = -Br, Yield: First cycle: 99% Second cycle: 86% Third cycle: 64%

Entry	X	R	Solvent	Base	Yield (%) ^b	TON ^c	TOF (h^{-1})
1	Br	Н	o-Xylene	K ₂ CO ₃	72	95	24
2	Br	Н	DMF	K ₂ CO ₃	56	74	19
3 ^d	Br	Н	H_2O	K ₂ CO ₃	42	55	14
4	Br	Н	Toluene	K ₂ CO ₃	64	85	21
5	Br	Н	o-Xylene	КОН	99	136	34
6	Br	Н	o-Xylene	Na ₂ CO ₃	12	16	4
7	Br	NO_2	o-Xylene	K_3PO_4	30	40	10
8	Br	OMe	o-Xylene	КОН	99	136	34
9	Br	CN	o-Xylene	КОН	99	136	34
10	Br	NO_2	o-Xylene	КОН	99	136	34
11 ^e	Ι	Н	o-Xylene	КОН	99	136	68

^aConditions: bromobenzene (1 mmol), 4-tolylboronic acid (1.5 mmol), K₂CO₃ (0.95 mmol), solvent (2 mL), Catalyst 3 (0.76 mol%), 90°C, 4 hr.

^bThe yield was calculated by the ¹H NMR spectrum with the internal standard of mesitylene.

^cTurnover number (TON) was determined from the quantity of product and catalyst.

^dTBAB (2 mmol).

^e2 hr.

in *o*-xylene (Table 5, Entry 5). However, the TON of Catalyst 3 for Suzuki-Miyaura reaction should be higher because the different substituents on bromobenzene did not affect the TON values of reactions mediated by Catalyst 3 (Table 5, Entries 8–10), and the reaction of 4-tolyboronic acid and iodobenzene also showed a TON value of 136 but the conversion approached 99% with a shorter time of 2 hr (Table 5, Entry 11) Nevertheless, the decreased yield with recycling times indicated that the Catalyst 3 was lost during the recycling test. Therefore, we decided to design the next coordinative monomer rather than identify the highest TON of Catalyst 3 or measure the Pd leakage (Figure 4).

2.6 | Suzuki-Miyaura reaction catalyzed by poly(MVPhDPy-co-NIPAM)-Pd(OAc)₂

The loss of poly(DPyVPhE-*co*-NIPAM)-Pd(OAc)₂ was attributed to the hydroxyl group on DPyVPhE and thus we converted the hydroxyl group of DPyVPhE to the methoxyl group via the methylation to generate the new coordinative monomer of MVPhDPy^[25] for higher catalytic activity (Scheme 6). The conversion from DPyVPhE to MVPhDPy could approach 72% within 5.5 hr and was recognized by the ¹H NMR spectrum (Figure S4). The ORTEP diagram further confirmed that the structures of DPyVPhE and MVPhDPy are quite similar and could be only differentiated by the hydroxyl group and the methoxyl group (Figure 5). Given by the experience of Catalyst 3, the polymer backbone was obtained from free radical polymerization of



FIGURE 4 ORTEP diagram of DPyVPhE-Pd(OAc)₂ depicted with ellipsoids at the 50% probability. Selected bond lengths (Å) and angles (°) for DPyVPhE-Pd(OAc)₂: Pd-N(1) 2.004(3), Pd-N(2) 2.009 (3), Pd-O(1) 2.016(2), Pd-O(3) 2.016(2), O(5)-C(1) 1.409(4), C(19)-C (20) 1.306(6), N(1)-Pd-N(2) 86.68(11), N(1)-Pd-O(1) 175.59(11), N (2)-Pd-O(1) 92.76(10), N(1)-Pd-O(3) 92.02(11), N(2)-Pd-O(3) 170.78 (11), O(1)-Pd-O(3) 89.22(10), C(21)-O(1)-Pd 119.9(2), C(23)-O(3)-Pd 123.5(3), C(2)-N(1)-Pd 121.0(2), C(6)-N(1)-Pd 119.5(2), C(11)-N(2)-Pd 120.2(2), and C(7)-N(2)-Pd 119.9(2)

MVPhDPy and NIPAM with the condition of (AIBN)₀/ (MVPhDPy)₀/(NIPAM)₀ = 1/1.6/8.2 in toluene at 60°C for 48 hr (Scheme 7). The polymeric product was characterized by GPC (M_n = 6,300 g/mL, D = 5.22) as well as ¹H NMR (Figure 6) and then reacted with Pd(OAc)₂ to form the brown powder of heterogeneous catalyst of poly (MVPhDPy-*co*-NIPAM)-Pd(OAc)₂ (Catalyst 4). The palladium content of Catalyst 4 was also measured by ICP-AES to be 10.2% (0.51 mg, MVPhDPy /Pd = 2.7, 6 Pd per polymer chain).

The heterogeneous catalyst of poly(MVPhDPy-*co*-NIPAM)-Pd(OAc)₂ was then used to mediate the Suzuki-Miyaura reaction of 4-tolyboronic acid and bromobenzene derivatives with different bases in o-xylene for the optimized conditions (Table 6). Five bases were used and the reaction with Cs₂CO₃ showed the highest yield as 99%, followed by



SCHEME 6 Synthesis of MVPhDPy monomer from DPyVPhE via methylation



FIGURE 5 ORTEP diagram of MVPhDPy depicted with ellipsoids at the 50% probability. Selected bond lengths (Å) and angles (°) for MVPhDPy: O(1)-C(21) 1.4220(16), O(1)-C(1) 1.4340(14), N (1)-C(7) 1.3371(16), N(1)-C(11) 1.3374(18), N(2)-C(2) 1.3313(16), N (2)-C(6) 1.3360(18), C(19)-C(20) 1.303(2), C(21)-O(1)-C(1) 115.76 (9), C(7)-N(1)-C(11) 117.28(12), C(2)-N(2)-C(6) 117.08(11), O(1)-C (1)-C(7) 105.55(9), O(1)-C(1)-C(2) 109.17(9), O(1)-C(1)-C(12) 112.27 (10), N(2)-C(2)-C(3) 122.31(12), N(2)-C(2)-C(1) 118.42(10), N(2)-C (6)-C(5) 124.66(13), N(2)-C(6)-H(6) 117.7, N(1)-C(7)-C(8) 122.81 (12), N(1)-C(7)-C(1) 114.67(10), N(1)-C(11)-C(10) 123.87(14), N(1)-C(11)-H(11) 118.1, O(1)-C(21)-H(21A) 109.5, O(1)-C(21)-H(21B) 109.5, and O(1)-C(21)-H(21C) 109.5



FIGURE 6 The (a) ¹H NMR spectrum and (b) GPC traces of poly(MVPhDPy-*co*-NIPAM)

the reaction with KOH, K₂CO₃, N(C₂H₅)₃, and Na₂CO₃ (Table 6, Entries 1-5). The versatility of Catalyst 4 was demonstrated by the mediation of the Suzuki-Miyaura reaction with varied bromobenzene derivatives, which all achieved high yield with a TON larger than 200 (Table 6, Entries 6-11). After the reaction of 4-tolyboronic acid and bromobenzene, Catalyst 4 was recycled by simple filtration and then used to mediate the same reaction for another four times. The leakage of palladium in the recycling test was not detectable and the yield was higher than 94%, implying that the structure of MVPhDPy was more stable and thus the heterogeneous catalyst of poly(MVPhDPy-co-NIPAM)-Pd (OAc)₂ can be applied to the Suzuki-Miyaura reaction under a harsh condition. The highest TON value for Catalyst 4 was then evaluated by the reaction of 4-tolyboronic acid and iodobenzene as 5,260 (Table 6, Entry 12).

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The mechanism of the Suzuki-Miyaura reaction mediated by these polymeric heterogeneous catalysts is proposed to be similar to that reported for homogeneous catalysis (Scheme 8).^[28–30] The Pd(II) coordinated by the polymer backbone is transformed into Pd(0) and reacts with aryl halide via oxidative addition. After the replacement of halide by the nucleophile, the aryl group on 4-tolyboronic acid exchanges with nucleophile. Two aryl groups on the Pd(II) center then form the product via the reduction elimination and Pd(II) is reduced to Pd(0) to start the next catalytic cycle. The palladium species before and after the reaction have been identified by X-ray photoelectron spectroscopy (Figure 7), which demonstrated that Pd(II) is the major species but the accumulation of Pd(0) could be observed after five times recycling. The trend in the substituent effect and the occurrence of accumulated Pd(0) matched the observation of the typical mechanism of the Suzuki-Miyaura reaction.^[30]

3 | EXPERIMENTAL

3.1 | Materials

Solvents were dried by refluxing for 24 hr with sodium/benzophenone (Tetrahydrofuran [THF], ether) or CaH₂ (toluene, CH₂Cl₂, pyridine, DMF, CH₃CN, o-xylene). 2-bromopyridine (>99%, Aldrich), n-BuLi (2.5 M in hexanes, Aldrich), 2-pyridinecarboxaldehyde (>99%, Aldrich), sodium hydride (60%, ACROS), acryloyl chloride (96%, Alfa Aesar), 2,2'-azobis(isobutyronitrile) (AIBN, Showa), benzylalcohol (99%, ACROS), 2,2,6,6-Tetramethyl-1-piperidinyloxy (98%, Alfa Aesar), KOH (85%, Aldrich), phenylethanol (98%, Aldrich), and potassium carbonate (K_2CO_3) (99%, Aldrich) were used as received. Copper(II) bromide $(CuBr_2)$, copper(II) trifluoromethanesulfonate (Cu(OTf)₂), palladium acetate (Pd $(OAc)_{2}$), 4-tolyboronic acid, bromobenzene, 4-bromobenonitrile, 4-bromoanisole, indole, and methyl

TABLE 6 Suzuki-Miyaura reaction catalyzed by poly(MVPhDPy-*co*-NIPAM)-Pd(OAc)₂ (Catalyst 4) with varied solvents and bromobenzene derivatives^a



R = -H, Yield, Pd leakage^b: First cycle: 99%, 0%. Fourth cycle: 98%, 0% Second cycle: 99%, 0%. Fifth cycle: 94%, 0% Third cycle: 99%, 0%

R = -CN, Yield, Pd leakage: First cycle: 99%, 0%. Fourth cycle: 99%, 0.2% Second cycle: 99%, 0%. Fifth cycle: 99%, 0.2%

Third cycle: $99\%,\,0\%$

Entry	X	R	Time (hr)	Base	Yield (%) ^c	TON ^d	$TOF(h^{-1})$
1	Br	Н	5	Na ₂ CO ₃	Trace	_	_
2	Br	Н	5	K ₂ CO ₃	68	141	28
3	Br	Н	5	KOH	86	179	36
4	Br	Н	5	Cs ₂ CO ₃	99	208	42
5	Br	Н	5	$N(C_2H_5)_3$	11	23	5
6	Br	OMe	5	Cs ₂ CO ₃	98	206	41
7	Br	NH ₂	5	Cs ₂ CO ₃	98	206	41
8	Br	CH ₃	5	Cs ₂ CO ₃	99	206	41
9	Br	CH(CH ₃) ₂	4	Cs ₂ CO ₃	99	208	52
10	Br	NO ₂	4	Cs ₂ CO ₃	99	208	52
11	Br	CN	4	Cs ₂ CO ₃	99	208	52
12 ^e	Ι	Н	20	Cs ₂ CO ₃	95	5,260	263

^aConditions: bromobenzene (1 mmol), 4-tolylboronic acid (1.5 mmol), Catalyst 4 (0.48 mol%), base (0.95 mmol), *o*-xylene (2 mL), 90°C.

^bMetal leakage was determined by ICP-AES.

^cThe yield was calculated by the ¹H NMR spectrum with the internal standard of mesitylene.

^dTurnover number (TON) was determined from the quantity of product and catalyst.

eCatalyst 4 (0.018 mol%).



SCHEME 8 Proposed mechanism of the Suzuki-Miyaura reaction



FIGURE 7 XPS, X-ray photoelectron spectroscopy spectrum of Catalyst 4 in fresh and after the fifth mediation of the Suzuki-Miyaura reaction

3,3,3-trifluoropyruvate were purchased from Alfa Aesar and used as received without further purification. Deuterated solvents (Aldrich) were dried over molecular sieves before use.

3.2 | Instrumentation

¹H NMR and ¹³C NMR spectra were recorded by Mercury-400 spectrometers, using deuterated solvents (CDCl₃) obtained from Aldrich and internal standard of mesitylene (0.1 mL) if necessary. The ¹H NMR spectrum was used to characterize the DPyMA and PDPyMA as well as calculate the conversion of reactions. Chemical shifts were calibrated by δ 7.24 ppm (CDCl₃). The Ultraviolet-vis spectrum was measured by a SHIMADZU UV-1800 instrument from 1,100 to 190 nm. GPC was carried out by the DMF-LiBr eluent using the Waters 600 liquid chromatograph equipped with a 101 refractive index detector and styragel HR columns (HR2; HR5). The signal was collected by a DIONEX Shodex RI-101 refractometer (RI) detector and an UltiMate 3000 variable wavelength detector operated at 254 nm for the DMF system. The calibration was based on narrow linear poly(ethylene oxide) standard for the DMF system. The metal quantity of heterogeneous catalysts and residual solutions were analyzed on an Agilent 725 ICP-AES.

3.3 | Synthesis of di(pyridin-2-yl)methanol

Di(pyridin-2-yl)methanol (BPyOH) was synthesized by following the reported procedure.^[51] 2-bromopyridine (9.5 mL, 100 mmol) and n-BuLi (62.5 mL, 100 mmol, 1.6 M in hexane) were mixed at -78° C in anhydrous Et₂O (200 mL) under a N₂ atmosphere for 20 min. The reaction was then quenched with 2-pyridinecarboxaldehyde (9.5 mL, 100 mmol) at the same temperature. After reacting for 30 min, the mixture was diluted by 2.0 M HCl (160 mL) and then pH value of the mixture was tuned to 8 by solid NaOH. The solution was then extracted with Et₂O. The organic layer was washed by brine and dried over MgSO₄. The residual mixture was purified by chromatography using silica gel (petroleum ether-EtOAc) to afford BPyOH (10.8 g, 60%). ¹H NMR (400 MHz, CDCl₃) δ 8.54 (d, 2H), 7.64 (t, J = 7.7 Hz, 2H), 7.51 (d, J = 7.9 Hz, 2H), 7.17 (t, J = 7.4 Hz, 2H), and 5.87 (s, 1H), 5.78 (br, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 160.72, 148.19, 136.85, 122.58, 121.13, and 75.18. Anal. Calcd. (found) for C₁₁H₁₀N₂O: N, 15.04 (14.94); C, 70.95 (70.56); and H, 5.41 (5.32).

3.4 | Synthesis of DPyMA

A 60 mL THF solution of 9.0 g (48 mmol, 1.0 eq.) BPyOH was added to another 60 mL THF solution of 2.3 g (96 mmol, 2.0 eq.) NaH at room temperature under N_2 .^[25]

After H₂-evolution stopped (1.5 hr), 4.66 mL (57.6 mmol, 1.2 eq.) of acryloyl chloride was added slowly into the solution at 0°C followed by the addition of NH₄Cl to quench the excess NaH after 60 min. The crude product was partitioned into CH₂Cl₂ and water layers. The aqueous layer was washed twice with CH₂Cl₂ and all CH₂Cl₂ solution was dried by anhydrous MgSO₄. The product of DPyMA was obtained after chromatography ($CH_2Cl_2/MeOH = 15/1$) as a slightly yellow oil (3 g, 26%). ¹H NMR (400 MHz, CDCl₃) δ 8.54 (d, 2H), 7.68 (t, J = 12.8 Hz, 2H), 7.57 (d, J = 7.8 Hz, 2H), 7.18 (t, 2H), 6.96 (s, 1H), 6.51 (d, 1H), 6.30 (ddd, J = 17.3 Hz, 1H), and 5.89 (d, 1H). ¹³C NMR (101 MHz, CDCl₃) & 157.9, 149.5, 136.8, 131.9, 128.0, 122.9, 122.0, 78.8, 77.3, and 77. Anal. Calcd. (found) for C₁₄H₁₂N₂O₂: N, 11.66 (11.59); C, 69.99 (69.55); and H, 5.03 (4.98).

3.5 | Synthesis of DPyVPhE

A 60 mL THF solution of 9.0 g (48 mmol, 1.0 eq.) BPyOH was added to another 60 mL THF solution of 2.3 g (96 mmol, 2.0 eq.) NaH at room temperature under N₂.^[43] After H₂-evolution stopped (1.0 hr), 8.27 mL (57.6 mmol, 1.2 eq.) of 4-vinylbenzyl chloride was added slowly into the solution at 0°C followed by the addition of NH₄Cl to quench the excess NaH after 5 hr. The crude product was partitioned into CH₂Cl₂ and water layers. The aqueous layer was washed twice with CH₂Cl₂ and all CH₂Cl₂ solution was dried by anhydrous MgSO₄. The product of DPyVPhE was obtained after chromatography (Hexane/ EtOAc = 7/1) as a slightly yellow oil (10.4 g, 72%). ¹H NMR (400 MHz, CDCl₃) δ 8.48 (ddd, J = 4.9, 1.8, 0.8 Hz, 2H), 7.87 (dt, J = 8.0, 1.0 Hz, 2H), 7.62 (td, J = 7.8, 1.8 Hz, 2H), 7.16-7.05 (m, 4H), 6.95 (d, J = 8.2 Hz, 2H), 6.59 (dd, J = 17.6, 10.9 Hz, 1H), 6.43 (s, 1H), 5.61 (dd, J)J = 17.6, 1.0 Hz, 1H, 5.11 (dd, J = 10.9, 1.0 Hz, 1H), and 3.67 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 162.65 (s, 2H), 147.26 (s, 7H), 136.76 (d, J = 5.5 Hz, 12H), 135.22 (s, 1H), 130.83 (s, 7H), 125.32 (s, 7H), 122.06 (s, 8H), 121.35 (s, 7H), 112.79 (s, 4H), 78.36 (s, 1H), and 47.36 (s, 4H).

3.6 | Synthesis of MVPhDPy

A 85 mL THF solution of 11.9 g (40 mmol, 1.0 eq.) DPyVE was added to another 85 mL THF solution of 3.84 g (160 mmol, 2.0 eq.) NaH at room temperature under N₂.^[25] After H₂-evolution had stopped (2.5 hr), 3.0 mL (48 mmol, 1.2 eq.) of CH₃I was added slowly into the solution at 0°C followed by the addition of NH₄Cl to quench the excess NaH after 5.5 hr. The crude product was partitioned into CH₂Cl₂ and water layers. The aqueous layer was washed

twice with CH₂Cl₂ and all CH₂Cl₂ solution was dried by anhydrous MgSO₄. The product of MVPhDPy was obtained after chromatography (Hexane/EtOAc = 4/1) as a slightly yellow oil (9.1 g, 72%). ¹H NMR (400 MHz, CDCl₃) δ 8.58 (ddd, J = 5.8, 1.8, 0.9 Hz, 2H), 7.52 (td, J = 7.8, 1.7, 2H), 7.35 (dt, J = 8.0, 1.0 Hz, 2H), 7.16–7.06 (m, 4H), 6.77 (d, J = 8.2 Hz, 2H), 6.58 (dd, J = 22.6, 10.9 Hz, 1H), 5.60 (d, J = 17.6 Hz, 1H), 5.11 (d, J = 10.7 Hz, 1H), 3.99 (s, 2H), and 3.27 (s, 3H).¹³C NMR (101 MHz, CDCl₃) δ 162.66 (s, 2H), 148.46 (s, 10H), 137.25 (s, 2H), 136.69 (s, 5H), 136.15 (s, 10H), 135.00 (s, 1H), 130.28 (s, 9H), 125.34 (s, 9H), 122.19 (s, 11H), 121.87 (s, 11H), 112.73 (s, 6H), 86.18 (s, 1H), 51.18 (s, 3H), and 38.24 (s, 6H).

3.7 | Synthesis of PDPyMA

A DMF solution (15 mL) of DPyMA (3.00 g, 12.50 mmol) and AIBN (0.21 g, 1.25 mmol) was heated to 60° C and stirred for 36 hr. The residual liquid including monomer and DMF was removed under vacuum. The pale yellow powder was dissolved in CH₂Cl₂ (10.0 mL) and then recrystallized by the addition of hexane (100.0 mL).

3.8 | Synthesis of poly(1,1-di(pyridin-2-yl)-2-(4-vinylphenyl)Ethan-1-ol) (PDPyVPhE)

A toluene solution (11.5 mL) of DPyVPh (1.20 g, 4.00 mmol) and AIBN (0.07 g, 0.40 mmol) was heated to 60° C and stirred for 48 hr. The residual liquid including monomer and toluene was removed by vacuum. The white powder was dissolved in CH₂Cl₂ (10.0 mL) and then recrystallized by the addition of hexane (100.0 mL).

3.9 | Synthesis of poly(DPyVPhE-co-NIPAM)

A toluene solution (34.3 mL) of DPyVPhE (1.20 g, 4.00 mmol), NIPAM (0.91 g, 8.00 mmol), and AIBN (0.19 g, 1.20 mmol) was heated to 60° C and stirred for 48 hrs. The residual liquid including monomer and toluene was removed by vacuum. The white powder was dissolved in CH₂Cl₂ (20.0 mL) and then recrystallized by the addition of hexane (200.0 mL).

3.10 | Synthesis of poly(MVPhDPy-co-NIPAM)

A toluene solution (61.7 mL) of MVPhDPy (1.14 g, 3.60 mmol), NIPAM (2.04 g, 18.00 mmol), and AIBN (0.35 g, 2.20 mmol) was heated to 60° C and stirred for 48 hr. The residual liquid including monomer and toluene was removed by vacuum. The white powder was dissolved

in CH_2Cl_2 (20.0 mL) and then recrystallized by the addition of hexane (200.0 mL).

3.11 | Synthesis of DPyMA-coordinated metal complexes

The synthesis of monomeric complex of [(DPyMA)CuBr $(\mu$ -Br)]₂ was described as an example. A CH₂Cl₂ solution of DPyMA (0.54 g, 2.20 mmol) and CuBr₂ (0.25 g, 1.10 mmol) was stirred for 24 hr at room temperature. The solution was then vacuumed to obtain the precipitation of black powder as the product of DPyMA-CuBr₂.

3.12 | Synthesis of PDPyMA-Pd(OAc)₂ (Catalyst 1a)

PDPyMA (0.24 g, DPyMA to $Pd(OAc)_2 = 1:1$) and $Pd(OAc)_2$ (0.22 g, 1.00 mmol) were mixed in a CH_2Cl_2 solution (15 mL) at room temperature for 24 hr. PDPyMA- $Pd(OAc)_2$ was gradually precipitated during the reaction and was obtained by filtration.

3.13 | Synthesis of PDPyMA-Cu(OTf)₂ (Catalyst 1b)

PDPyMA (0.36 g, DPyMA to $Cu(OTf)_2 = 1.5:1$) and $Cu(OTf)_2$ (0.48 g, 1.00 mmol) were mixed in a CH_2Cl_2 solution (20 mL) at room temperature for 24 hr. PDPyMA- $Cu(OTf)_2$ was gradually precipitated during the reaction and was obtained by filtration.

3.14 | Synthesis of PDPyVPhE-Pd(OAc)₂ (Catalyst 2)

PDPyVPhE (0.30 g, DPyVPhE to $Pd(OAc)_2 = 1:1$) and $Pd(OAc)_2$ (0.22 g, 1.00 mmol) were mixed in a CH_2Cl_2 solution (15 mL) at room temperature for 24 hr. PDPyVPhE-Pd(OAc)₂ was gradually precipitated during the reaction and was obtained by filtration.

3.15 | Synthesis of poly(DPyVE-co-NIPAM)-Pd(OAc)₂ (Catalyst 3)

Poly(DPyVPhE-*co*-NIPAM) (0.87 g, DPyVPhE to $Pd(OAc)_2 = 1:1$) and $Pd(OAc)_2$ (0.22 g, 1.00 mmol) were mixed in a CH_2Cl_2 solution (15 mL) at room temperature for 24 hr. Poly(DPyVPhE-*co*-NIPAM)-Pd(OAc)_2 was gradually precipitated during the reaction and was obtained by filtration.

3.16 | Synthesis of poly(MVPhDPy-co-NIPAM)-Pd(OAc)₂ (Catalyst 4)

Poly(MVPhDPy-*co*-NIPAM) (0.88 g, MVPhDPy to $Pd(OAc)_2 = 1:1$) and $Pd(OAc)_2$ (0.22 g, 1.00 mmol) were mixed in a CH_2Cl_2 solution (15 mL) at room temperature for 24 hr. Poly(MVPhDPy-*co*-NIPAM)-Pd(OAc)_2 was gradually precipitated during the reaction and was obtained by filtration.

3.17 | General process for the Suzuki reaction

The catalyst (0.01 g), bromobenzene (1.00 mmol), 4-tolyboronic (1.50 mmol), and various base (0.95 mmol) were mixed in various solvents (2 mL) at 90°C for 4 hr. The conversion was calculated by the ¹H NMR and the internal standard is mesitylene (0.1 mL).

The highest TON was obtained by the reaction of catalyst (0.018 mol%), iodobenzene (1.00 mmol), 4-tolyboronic (1.50 mmol), and Cs2CO3 (0.95 mmol) in o-xylene (2 mL) at 90°C for 20 hr. The conversion was calculated by ${}^{1}\text{H}$ NMR with the internal standard of mesitylene (0.1 mL).

3.18 | General process for Friedel-Craft alkylation

The catalyst (0.50 g), indole (0.55 mmol), and methyl 3,3,3-trifluoropyruvate (0.50 mmol) were mixed in ether (2 mL) at 0°C for 20 hr. The conversion was calculated by the ¹H NMR with the internal standard of mesitylene (0.1 mL).

4 | CONCLUSIONS

Four coordinative polymers were developed for the heterogeneous catalysis of the Suzuki-Miyaura reaction and Friedel-Crafts alkylation. Catalysts 1a and 1b, which are insoluble powders with Pd(OAc)₂ and Cu(OTf)₂, can mediate the Suzuki-Miyaura reaction and Friedel-Crafts alkylation, respectively. However, the decomposition of Catalysts 1a and 1b due to the base limited their activity and thus DPyVPhE was synthesized for Catalysts 2 and 3. The TON of the Suzuki-Miyaura reaction was slightly increased by using Catalyst 2 but the recycling of the catalyst was still not completed. The introduction of NIPAM into the polymer backbone improved the activity, demonstrated by the higher TON of 136 in the Suzuki-Miyaura reaction mediated by Catalyst 3, yet the yield still decreased with the recycling time. MVPhDPy was obtained from the methylation of DPyVPhE and then copolymerized with NIPAM to form Catalyst 4 with Pd(OAc)₂. The Suzuki-Miyaura reaction of 4-tolyboronic acid and iodobenzene mediated by Catalyst 4 could approach the TON as 5,260. The Pd leakage was undetectable and the yield was constantly higher than 94% after 5 times recycling. In the literature, the range of TON for heterogeneous catalysis of Suzuki-Miyaura coupling is generally around 30 to 20,000.^[47,52–54] Although poly(MVPhDPy-*co*-NIPAM)-Pd(OAc)₂ showed a moderate catalytic activity, the ease of catalyst recycle and the little leakage of metal ions along with the versatility of polymeric platform that could coordinate with different metal ions to catalyze varied reactions provide this copolymer a great potential for future applications.

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REFERENCES

- Y. Uozumi, Immobilized Catalysts, Springer Verlag, Heidelberg, 2004, p. 77.
- [2] H. Wennemers, in *Highlights in Bioorganic Chemistry: Methods and Applications* (Eds: H. Wennemers, C. Schmuck), Wiley-VCH, Weinheim, **2004**, p. 436.
- [3] Y. Uozumi, T. Hayashi, in *Handbook of Combinatorial Chemistry: Drugs, Catalysts, Materials* (Eds: K. C. Nicolaou, R. Hanko, W. Hartwig), Wiley-VCH, Weinheim, **2002**, p. 531.
- [4] K. Mikami, M. Lautens, in *New Frontiers in Asymmetric Cataly-sis* (Eds: K. Mikami, M. Lautens), John Wiley & Sons, Hoboken, 2007, p. 275.
- [5] R. H. Crabtree, in *The Organometallic Chemistry of the Transition Metals* (Ed: R. H. Crabtree), John Wiley & Sons, Hoboken, 2009, p. 224.
- [6] T. Frenzel, W. Solodenko, A. Kirschning, in *Polymeric Materials in Organic Synthesis and Catalysis* (Ed: M. R. Buchmeiser), Wiley-VCH, Weinheim, **2003**, p. 201.
- [7] Z. Wang, G. Chen, K. Ding, Chem. Rev. 2008, 109, 322.
- [8] J. Lu, P. H. Toy, Chem. Rev. 2009, 109, 815.
- [9] K. Baer, M. Kraußer, E. Burda, W. Hummel, A. Berkessel, H. Gröger, Angew. Chem. Int. Ed. 2009, 48, 9355.
- [10] Y. Uozumi, Y. Yamada, Chem. Rec. 2009, 9, 51.
- [11] M. Lamblin, L. Nassar-Hardy, J. C. Hierso, E. Fouquet, F. X. Felpin, Adv. Synth. Catal. 2010, 352, 33.
- [12] S. M. Sarkar, Y. Uozumi, Y. M. A. Yamada, Angew. Chem. Int. Ed. 2011, 50, 9437.
- [13] S.-W. Kim, M. Kim, W. Y. Lee, T. Hyeon, J. Am. Chem. Soc. 2002, 124, 7642.
- [14] A. T. Bell, Science 2003, 299, 1688.
- [15] J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen, J. T. Hupp, *Chem. Soc. Rev.* **2009**, *38*, 1450.
- [16] Y. Liu, W. Xuan, Y. Cui, Adv. Mater. 2010, 22, 4112.
- [17] N. E. Leadbeater, M. Marco, Chem. Rev. 2002, 102, 3217.

- [19] J. Zhang, Y. Yan, L. Ren, C. Tang, Chem. Soc. Rev. 2016, 45, 5232.
- [20] B. S. Tucker, S. G. Getchell, M. R. Hill, B. S. Sumerlin, *Polym. Chem.* 2015, 6, 4258.
- [21] B. L. Sanchez-Gaytan, W. Cui, Y. Kim, M. A. Mendez-Polanco, T. V. Duncan, M. Fryd, B. B. Wayland, S. J. Park, *Angew. Chem. Int. Ed.* 2007, 119, 9395.
- [22] D. Astruc, F. Lu, J. R. Aranzaes, Angew. Chem. Int. Ed. 2005, 44, 7852.
- [23] A. Corma, H. Garcia, Chem. Rev. 2003, 103, 4307.
- [24] N. T. Phan, M. Van Der Sluys, C. W. Jones, Adv. Synth. Catal. 2006, 348, 609.
- [25] C. Wiles, P. Watts, S. J. Haswell, E. Pombo-Villar, *Tetrahedron* 2003, 59, 10173.
- [26] G. Martens, P. Rabe, N. Schwentner, A. Werner, *Phys. Rev. B* 1978, 17, 1481.
- [27] K. Waizumi, H. Masuda, H. Ohtaki, *Inorg. Chim. Acta* 1992, 192, 173.
- [28] G. A. Grasa, M. S. Viciu, J. Huang, C. Zhang, M. L. Trudell, S. P. Nolan, *Organometallics* **2002**, *21*, 2866.
- [29] E. A. B. Kantchev, C. J. O'Brien, M. G. Organ, Angew. Chem. Int. Ed. 2007, 46, 2768.
- [30] N. Miyaura, A. Suzuki, Chem. Rev. 1995, 95, 2457.
- [31] T. Ohmura, T. Awano, M. Suginome, J. Am. Chem. Soc. 2010, 132, 13191.
- [32] T. Yamamoto, Y. Akai, Y. Nagata, M. Suginome, Angew. Chem. Int. Ed. 2011, 50, 8844.
- [33] T. E. Barder, S. D. Walker, J. R. Martinelli, S. L. Buchwald, J. Am. Chem. Soc. 2005, 127, 4685.
- [34] P. Li, L. Wang, L. Zhang, G. W. Wang, Adv. Synth. Catal. 2012, 354, 1307.
- [35] G. A. Grasa, A. C. Hillier, S. P. Nolan, Org. Lett. 2001, 3, 1077.
- [36] O. Navarro, R. A. Kelly, S. P. Nolan, J. Am. Chem. Soc. 2003, 125, 16194.
- [37] J.-H. Li, W.-J. Liu, Y.-X. Xie, J. Org. Chem. 2005, 70, 5409.
- [38] Y. M. Kim, S. Yu, J. Am. Chem. Soc. 2003, 125, 1696.

- [39] D. A. Evans, K. R. Fandrick, H.-J. Song, K. A. Scheidt, R. Xu, J. Am. Chem. Soc. 2007, 129, 10029.
- [40] Y.-X. Jia, S.-F. Zhu, Y. Yang, Q.-L. Zhou, J. Org. Chem. 2006, 71, 75.
- [41] J. Zhou, M.-C. Ye, Z.-Z. Huang, Y. Tang, J. Org. Chem. 2004, 69, 1309.
- [42] M. P. Lyle, N. D. Draper, P. D. Wilson, Org. Lett. 2005, 7, 901.
- [43] M. T. Barros, A. I. Mouquinho, K. T. Petrova, M. D. Saavedra, J. C. Sotomayor, *Cent. Eur. J. Chem.* **2011**, *9*, 557.
- [44] B. Tao, D. W. Boykin, J. Org. Chem. 2004, 69, 4330.
- [45] S. Li, Y. Lin, J. Cao, S. Zhang, J. Org. Chem. 2007, 72, 4067.
- [46] M. Beygzadeh, A. Alizadeh, M. M. Khodaei, D. Kordestani, *Cat. Com.* 2013, 32, 86.
- [47] Y. M. A. Yamada, Chem. Pharm. Bull. 2005, 53, 723.
- [48] Y. M. A. Yamada, Y. Maeda, Y. Uozumi, Org. Lett. 2006, 8, 4259.
- [49] Y. M. A. Yamada, S. M. Sarkar, Y. Uozumi, J. Am. Chem. Soc. 2012, 134, 3190.
- [50] Y. M. A. Yamada, S. M. Sarkar, Y. Uozumi, J. Am. Chem. Soc. 2012, 134, 9285.
- [51] W. Mai, L. Gao, Synlett 2006, 2006, 2553.
- [52] M. Charbonneau, G. Addoumieh, P. Oguadinma, A. R. Schmitzer, *Organometallics* 2014, 33, 6544.
- [53] P. Zhang, Z. Weng, J. Guo, C.-C. Wang, *Chem. Mater.* 2011, 23, 5243.
- [54] I. Hussain, J. Capricho, M. A. Yawer, Adv. Synth. Catal. 2016, 358, 3320.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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