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covalently tethered on a thermo-responsive polymer

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Palladium-catalysed reactions in water using catalysts covalently tethered on a thermo-responsive polymer†

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Bidentate *N,N*-ligand moieties were covalently tethered on a RAFT agent by Hüisgen cycloaddition, and poly(*N*-isopropylacrylamide) (PNIPAAm) bearing the ligand moiety was obtained by living-radical polymerization using these RAFT agents. The polymer formed a palladium complex covalently immobilized at the terminus of each polymer chain. Palladium-catalysed Mizoroki–Heck and Suzuki–Miyaura cross coupling reactions proceeded in water with these polymer-immobilized Pd catalysts. The products were obtained in good yields and the aqueous layer containing the polymer catalysts could be reused. Electron microscopic analysis suggested that palladium nanoparticles formed during the reaction were responsible for the catalytic activity. Using an NNC-pincer Pd complex tethered on the polymer, the catalytic reaction was completed with 0.01 mol% of Pd loading. The aqueous solution could be reused 8 times, and a turnover number (TON) of up to 82 800 was achieved.

1. Introduction

In order to achieve sustainable development goals (SDGs), the development of environmentally friendly processes for organic synthesis is an urgent issue. In response to this growing demand, there has been increasing interest in organic reactions using water as a solvent. Transition metal-catalysed organic reactions have found practical utility due to their high effectiveness, although the majority of these reactions have been conducted in organic solvents. Recently, there has been a surge in reported examples of organic reactions carried out in water using organometallic catalysts.[1–5] For example, one of the authors (FYT) and his coworkers reported a water-soluble bipyridyl ligand, the transition metal complexes of which showed high catalytic activity in water.[6–10] Furthermore, systems that facilitate smooth reactions within micelles by employing surfactants have also been extensively studied.[11–25] However, the extraction of reaction products from aqueous reaction mixture often requires the use of organic solvents, which results in an increase in the *E*-factor.[26] Therefore, extraction solvents must

be reduced for achieving truly environmentally benign chemical reactions.

We previously reported the application of diblock copolymers that consist of poly(*N*-isopropylacrylamide) (PNIPAAm) and a hydrophilic polymer chain, as thermo-responsive surfactants for catalytic organic reactions in water. PNIPAAm is well-known for its thermo-responsive property. It shows a lower critical solution temperature (LCST) at 32 °C in water, thus it has been extensively studied as a thermo-responsive polymer materials. There have been many reports on its biomedical applications such as in drug delivery systems, as well as its mechanical applications.[27–44] PNIPAAm has also been applied to organic reaction processes, including metal-catalysed reactions. Most of these adopted cross-linked PNIPAAm gels,[45–61] whereas examples that use non-cross-linked PNIPAAm for organic synthesis are still rare.[62–70] We demonstrated that utilizing those polymer
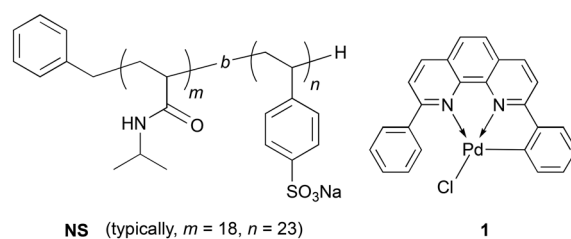
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Fig. 1 Thermo-responsive diblock copolymer **NS** and active Pd catalyst with NNC-pincer ligand.

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surfactants for catalytic reactions in water enabled more efficient extraction processes with smaller amounts of organic solvent.[63,71,72] In our previous reports, we studied palladium-catalysed reactions in water using the thermo-responsive polymer surfactants **NS** (Fig. 1). The use of **NS** allowed us to extract the products with less extraction solvent. We also disclosed that the aqueous layer containing the Pd catalyst could be reused several times.

In those studies, we reported palladium-catalysed reaction using various Pd sources including Pd complex **1**, which was reported as highly active catalyst.[73–75] When the aqueous layer containing **1** was reused for repeated catalytic reactions, however, the catalytic activity significantly decreased on the third reaction. This is probably because **1** is inherently lipophilic and was lost during the extraction procedure. In order to improve the reusability of the catalyst, we anticipated that the activity would be retained if the catalyst had thermo-responsive property. That is, the catalyst would stay in the hydrophobic micelle core during the reaction at high temperature, while it would move to the aqueous layer by cooling after the reaction (Fig. 2).

This idea of a thermo-responsive catalyst has also been described as a "thermo-morphic catalyst" or "thermo-regulated ligand".[76–79] There have been many reports on thermo-responsive ligands for catalysts, although many of which contain PEG-modified phosphine ligands. With regard to molecular catalysts covalently tethered on PNIPAAm chains, most of these were synthesized by copolymerization of "vinyl"-ligands and NIPAAm monomer or post-functionalization of PNIPAAm copolymers.[50,51,53,56,57,80,81] These polymers contained plural ligands in a single polymer chain, and their coordination to metal atoms caused cross-linking that resulted in aggregation and gelation. For reversible dissolution–dehydration of PNIPAAm chain in aqueous solutions, cross-linked structures should be avoided. One possible strategy to prevent cross-linking is to attach a single ligand to one of the polymer ends. For that purpose, RAFT agents bearing a ligand moiety can be employed. There have been some reports on bipyridyl,[82–85] terpyridyl[86,87] or phenanthroline[88–90] ligands that were covalently connected to RAFT agents such as thioesters. Although there are examples of PNIPAAm prepared with these RAFT agents, to the best of
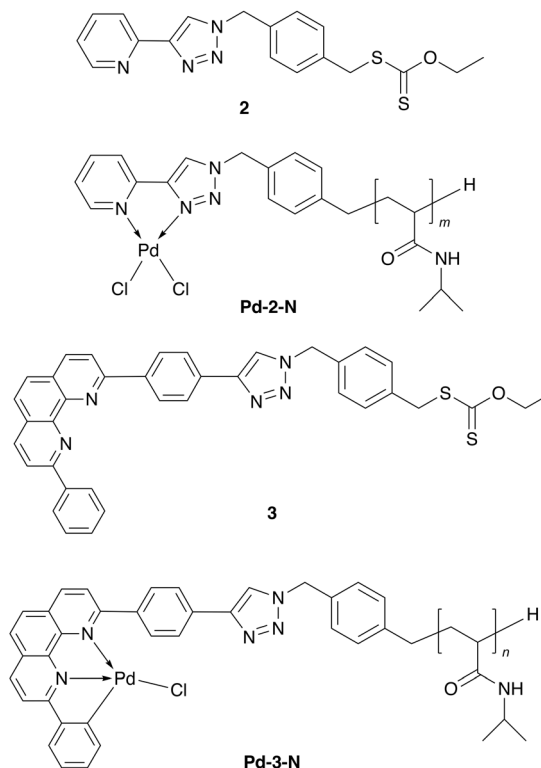

Fig. 3 Palladium complexes bearing a thermo-responsive polymer chain.

our knowledge, applications to catalytic reactions have not been disclosed.

Herein, we report the preparation of RAFT agents **2** and **3** (Fig. 3). We synthesized NIPAAm polymers bearing an *N,N*-ligand at the polymer end, and prepared their palladium complexes. The Pd-containing polymers **Pd-2-N** and **Pd-3-N** served as catalysts for the Mizoroki–Heck (M–H) reaction and Suzuki–Miyaura (S–M) coupling in water. The aqueous solution of **Pd-3-N** could be reused 8 times for M–H reactions and the turnover number (TON) reached 82 800.

2. Results and discussion

2.1. Synthesis of the RAFT agent 2 and catalyst-immobilized polymer Pd-2-N

We first studied the 2-pyridyl-1,2,3-triazole group as an *N,N*-bidentate ligand binding to the RAFT agent (Scheme 1). Due to its good accessibility, there have been many examples in which the 2-pyridyl-1,2,3-triazole ligand was attached to other materials such as mesoporous silica,[91–94] sugar,[95–97] *etc.* Samanta, Mandal and coworkers reported ATRP initiators bearing the 2-pyridyl-1,2,3-triazole ligand, synthesized PNIPAAm with them and applied their Ru and Cu complexes for catalytic reactions.[98,99] To the best of our knowledge, however, there have been no examples of RAFT agents that have an *N,N*-bidentate 2-pyridyl-1,2,3-triazole ligand moiety[100,101] and applications of ligand-tethered PNIPAAm for catalytic reactions are still rare.
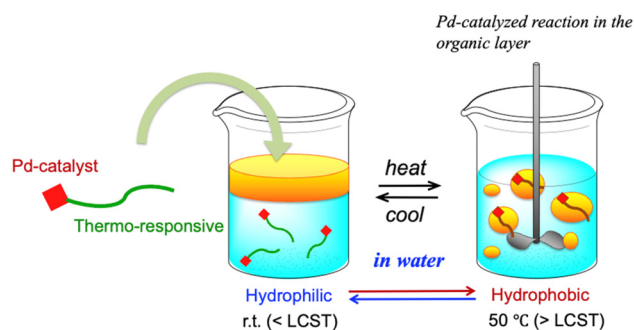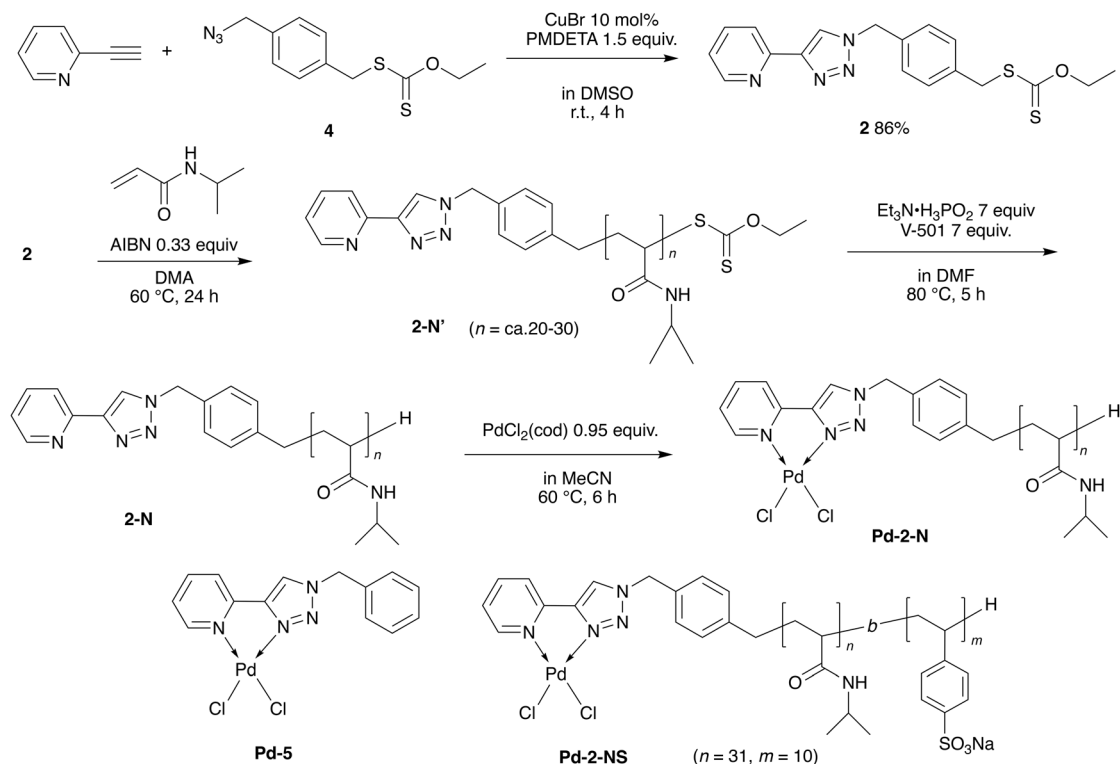

Fig. 2 "Thermo-responsive" catalyst.

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Scheme 1 Synthesis of thermo-responsive polymer catalysts.

The ethyl xanthogenate with an azide **4**[102] reacted with 2-ethynylpyridine to afford the N,N-ligand-tethered RAFT agent **2**. N-Isopropylacrylamide (NIPAAm) was polymerized by RAFT polymerization, followed by removal of the xanthogenate terminus by radical reaction to give the N,N-ligand tethered on PNIPAAm **2-N**. The polymer was then treated with PdCl$_2$(cod) to form a palladium complex at the end of the polymer chain (**Pd-2-N**). In the ^{1}H NMR spectrum of **2-N**, a singlet assignable to the triazole proton appeared at 8.0 ppm, while **Pd-2-N** showed broad signals above 9 ppm, suggesting the complexation of Pd metal. ICP analysis for Pd content was consistent with the expected values. **Pd-2-N** showed LCST behaviour in water solution; it was transparent at room temperature but turned opaque above 40 °C. For comparison, we also prepared a diblock copolymer **Pd-2-NS** that contains an anionic segment, and a small molecule of **Pd-5**, and tested their catalytic abilities.

2.2. Palladium-catalysed Mizoroki–Heck (M–H) reaction using the polymer catalyst Pd-2-N

The Mizoroki–Heck (M–H) reaction in water using the thermo-responsive polymer catalyst **Pd-2-N** was studied. We previously reported that copolymer **NS**, as a polymer surfactant, promoted the M–H reaction in water with PdCl$_2$(PPh$_3$)$_2$.[63,72] In this study, we also used **NS**. Iodoarene, alkene, base and catalyst **Pd-2-N** were added to an aqueous solution of **NS** at room temperature. Hydrazine hydrate as a reductant was then added and the mixture was heated at 70 °C with stirring. After 48 h, the
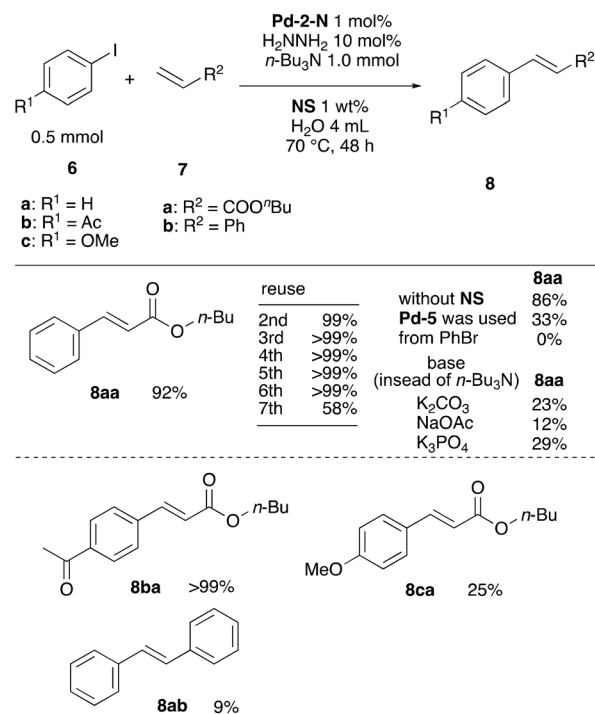

Chart 1 Mizoroki–Heck reactions in water using **Pd-2-N** in the presence of **NS**. Conditions: iodoarene (0.5 mmol), alkene (1.0 mmol), catalyst (typically 22.5 mg, containing 0.005 mmol Pd atom), hydrazine monohydrate (0.05 mmol), tri-n-butylamine (1.0 mmol), **NS** (40 mg), water (4 mL), 70 °C, 48 h. Yields were determined by ^{1}H NMR.

reaction mixture was cooled to 0 °C and ethyl acetate was added to extract the product (Chart 1). A few iodoarenes **6a–b** reacted with *n*-butyl acrylate (**7a**) to afford the product **8** in good yields, although 4-iodoanisole (**6c**) resulted in lower yield. As shown in our previous report, styrene (**7b**) was unsuitable under these reaction conditions. The yield of **8aa** was 86% when the reaction was carried out without adding **NS**, indicating the advantage of the polymer surfactant. The yield of **8aa** in 5 h in the presence of **NS** was 30%, while it was 64% in the absence of **NS**, implying that micelles formed by **NS** rather lowered the reaction rate. Higher yield of **8aa** in 48 h due to **NS** is presumably because it extended the lifetime of the catalyst. The extraction process was rapid when **NS** was added. The small molecular analogue **Pd-5** gave **8aa** in 33% yield, showing that the polymer pendant enhanced the catalytic performance in water. Use of inorganic bases resulted in lower yields, probably due to their dissolution in the aqueous layer.

Formation of Pd-black was not observed, while the color of the emulsion turned gray. Thus, we reused the aqueous layer of the reaction mixture containing **Pd-2-N**. The catalyst solution could be used more than 6 times but the yield decreased in the seventh cycle, and the TON reached 640 by 7 cycles.

We also synthesized the polymer catalyst **Pd-2-NS** in which the Pd catalyst was tethered on the "diblock copolymer" **NS**. It gave the M–H product **8aa** in 93% yield and the catalyst could be reused 5 times without use of the polymer surfactant **NS**. However, we found that the extraction process was somewhat troublesome; an emulsion was formed during the extraction, making it difficult to clearly separate the organic and aqueous layers. It was proposed that Pd metals could crosslink the polymer chains *via* sulfonate groups, which gave rise to aggregation of the polymers.[103] Thus, we decided to focus on the PNIPAAm "homopolymer" for further investigation.

2.3. Palladium-catalysed Suzuki–Miyaura (S–M) coupling using the polymer catalyst

Next, we applied **Pd-2-N** for Suzuki–Miyaura (S–M) coupling reactions (Chart 2). There have been many reports on S–M cross coupling conducted in water,[6,104–110] with some on PNIPAAm-immobilized ligands and their palladium complexes.[50,78,111] Applying surfactants for S–M reactions in water has also been well studied.[112,113] However, to the best of our knowledge, there has not been any study on S–M reactions in water using a molecular catalyst immobilized at the "soluble" PNIPAAm chain end. Various kinds of aryl boronic acids **9b–g** coupled with iodobenzene **6a** furnished the coupling products **10** in good to excellent yields using **Pd-2-N**. Phenylboronic acid (**9a**) reacted with aryl iodides **6c–e** bearing electron-donating groups to give the coupling products **10** in excellent yields, while **6c** gave **10ca** in 87% yield in the absence of the surfactant **NS**.
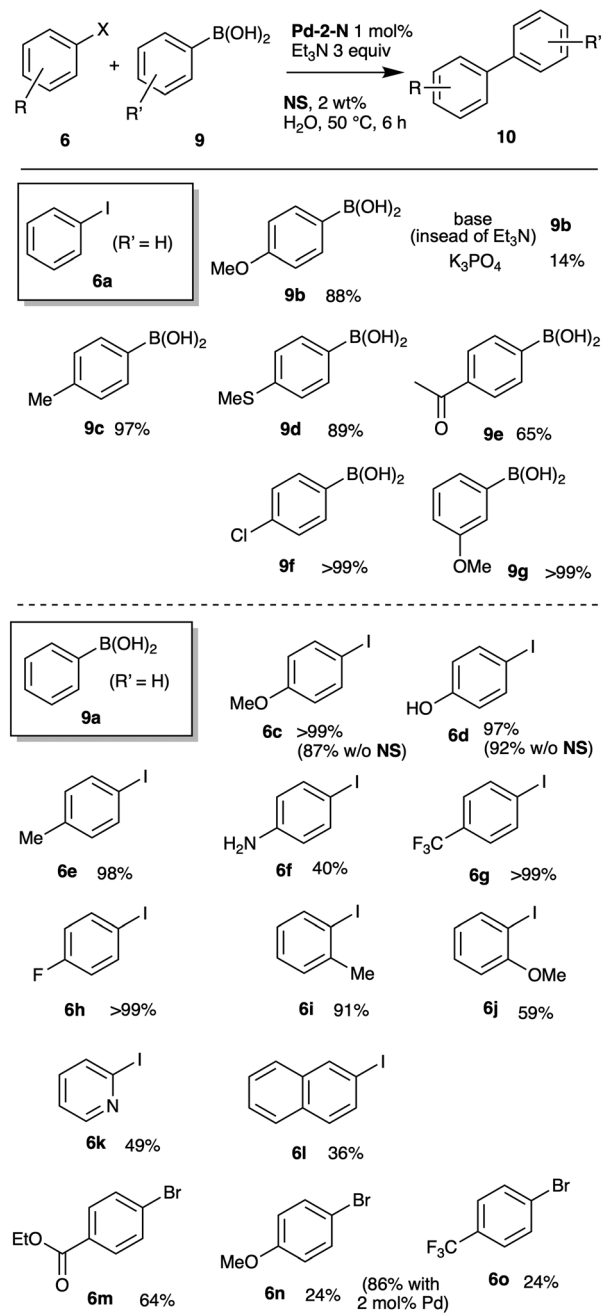
Chart 2 Suzuki–Miyaura coupling using **Pd-2-N** in water. Conditions: ArX **6** (0.5 mmol), ArB(OH)$_2$ **9** (0.75 mmol), **Pd-2-N** (containing 1 mol% Pd), Et$_3$N (1.5 mmol), **NS** (20 mg), H$_2$O (1 mL), yields of **10** were determined by ^{1}H NMR.

Electron-withdrawing groups **6g**, **h** gave the products in excellent yields. 4-Iodoaniline (**6f**) and 2-iodopyridine (**6k**) resulted in moderate yields, presumably due to competitive coordination to the metal. Sterically hindered *o*-substituted iodides afforded **10** in good yields (**6i**, **j**), while 2-iodonaphthalene (**6l**) gave the coupling product in a moderate yield. Aryl bromide with an electron-withdrawing group **6m** gave **10am** in good yield. Other bromides **6n**, **o** resulted in low yields, although **6n** and **9a** gave **10na** in 86%

yield when 2 mol% of Pd was used. Chloroarenes gave no products, even though the reaction was conducted at 80 °C. It has been reported that ligands such as SPhos, XPhos and NHC *etc.* were effective for S–M reactions of chloroarenes.[114–118] If a RAFT agent on which these ligands tethered successfully initiates polymerization of *N*-isopropylacrylamide, it may be effective for chloroarenes. When the small molecular analogue **Pd-5** was employed for the coupling between **6b** and **9a** in water in the presence of **NS**, it gave **10ba** in 17% yield, and **6m** gave **10ma** in 7% yield.

We also tested reuse of the aqueous catalyst solution. However, the second and third reuse gave the products in only 46 and 40% yields, whereas the first cycle was quantitative. Although the reason for the decrease in activity is yet unclear, borane waste contained in the aqueous layer might have disturbed the catalytic reaction.

2.4. STEM observation of the polymer catalysts

To shed light on the details of the catalytic performance of the polymer-tethered catalysts, the aqueous solution of **Pd-2-N** was observed by scanning transmission electron microscopy (STEM) (Fig. 4). STEM measurement of the **Pd-2-N** solution after a single run of M–H and S–M reactions showed the formation of Pd nanoparticles (PdNPs) with sizes ranging from 2 to 6 nm. Energy dispersive X-ray spectroscopy (EDX) indicated that the particles consisted of Pd element. Pd was also found in the matrix area, suggesting that some Pd atoms were attached on the ligand on the polymer.
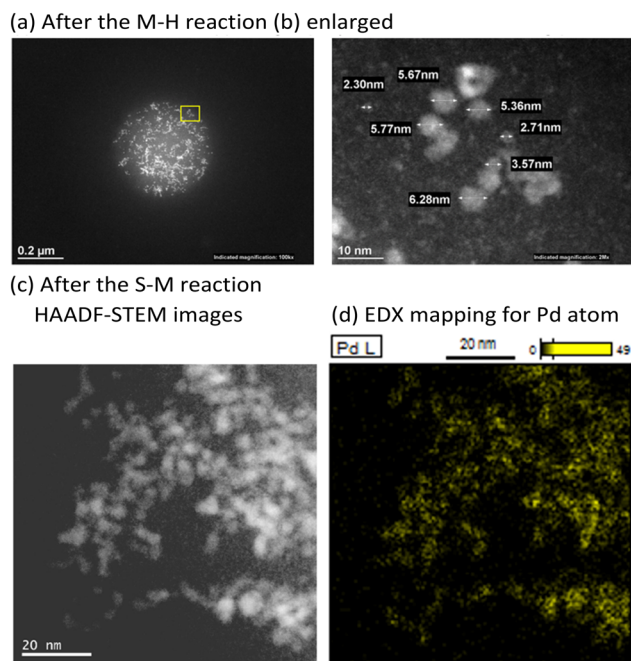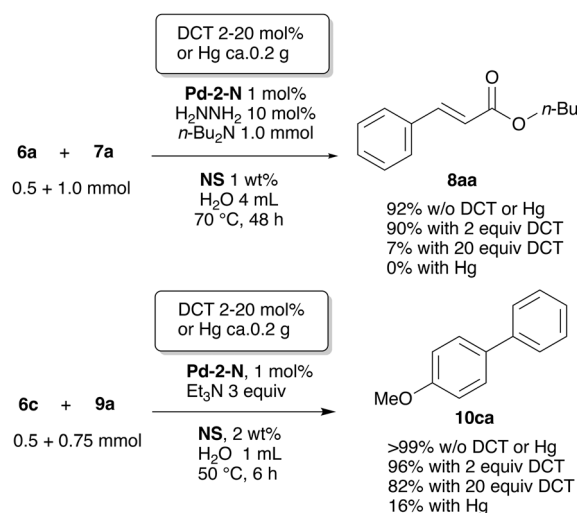

(a) After the M-H reaction (b) enlarged

(c) After the S-M reaction HAADF-STEM images

(d) EDX mapping for Pd atom

Fig. 4 STEM images of the **Pd-2-N** in the aqueous layer; (a and b) after the M–H reaction, (c and d) after the S–M reaction; (d) shows EDX mapping for Pd.

2.5. DCT test and mercury test

In order to obtain information on the catalytically active species, we carried out the Crabtree DCT test[119] and mercury test. Dibenzo[*a,e*]cyclooctene (DCT) serves as catalyst poison for the homogeneous system due to the strong coordination ability. Despite the addition of 2 equiv. of DCT per Pd, both the M–H and S–M reactions gave the corresponding products in good yields (Scheme 2). Addition of one drop of mercury, on the other hand, resulted in a significant decrease in the product yields. These results suggested that PdNPs formed in the system are predominantly responsible for the catalytic ability. Formed palladium nanoparticles were presumably stabilized by the PNIPAAm structure.[54,68] It is noteworthy that addition of 20 equiv. of DCT brought about a decrease in the product yield for M–H reactions (7%), while it did not affect the S–M reactions very much (82%). These results imply that the Pd complex in homogeneous fashion also plays a certain role, such as serving as a reservoir for PdNPs, particularly in M–H reactions.[74]
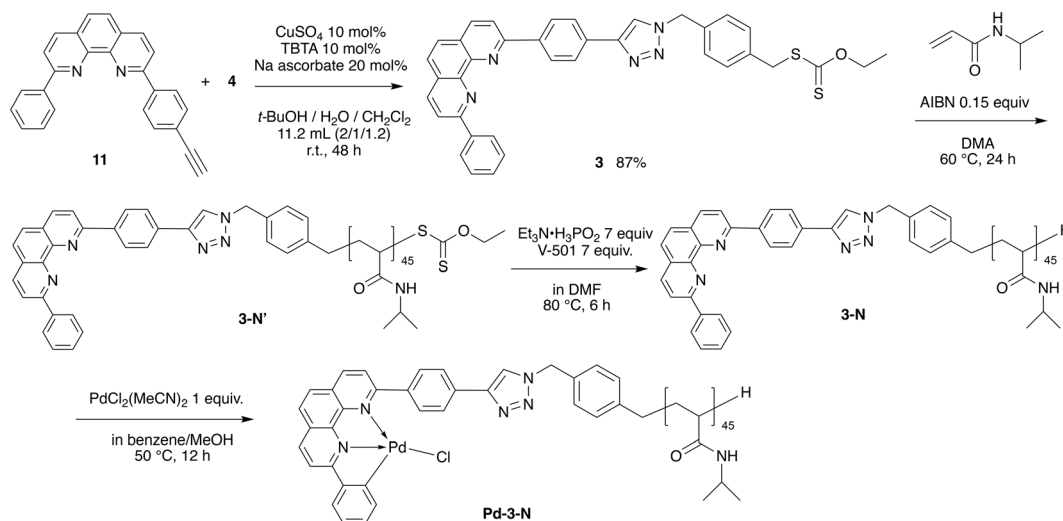
2.6. Polymer-immobilized NNC-pincer Pd complex

Uozumi and coworkers reported that the palladium complex of NNC-pincer type ligand **1** showed remarkably high catalytic activity for cross coupling reactions.[73–75,120] We previously reported that **1** served as an excellent catalyst in water using thermo-responsive polymer micelles, and that reuse of the aqueous catalyst solution reached TON of 7800.[72] However, **1** was gradually lost in extraction when the catalyst was reused. Therefore, we synthesized novel RAFT agent **3** in which the NNC-pincer ligand is covalently tethered on a RAFT agent moiety (Scheme 3).[88] The phenanthroline-based NNC-pincer ligand with an ethynyl group **11** was coupled with **4** to afford **3**. PNIAAm was polymerized using **3** followed by removal of the xanthogenate terminus to give the polymer **3-N**, which furnished palladium complex **Pd-3-N** by treatment with PdCl$_2$(MeCN)$_2$.

Scheme 2 DCT and mercury test for the catalytic reactions.

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Scheme 3 Preparation of thermo-responsive NNC-pincer Pd complex.

2.7. M–H reactions using Pd-3-N in water

We tested the polymer tethered NNC-Pd complex **Pd-3-N** for M–H reactions in water in the presence of the polymer surfactant **NS**. Various substrates afforded the coupling products with 0.1 mol% Pd catalyst in good yields (Chart 3). In the reactions with *n*-butyl acrylate (**7a**), aryl iodides **6** furnished alkenyl arenes **8** in excellent yields regardless of electron-withdrawing groups (**6b, g, p**) or electron-donating groups (**6c, e**). 1-Iodonaphthalene (**6q**) gave **8qa** quantitatively, while sterically hindered 2-iodotoluene **6i** gave **8ia** in 50% yield. Bromobenzene resulted in disappointing yield. *tert*-Butyl acrylate (**7c**) and *N*-isopropylacrylamide (**7d**) quantitatively furnished **8ac** and **8ad**, respectively, although 2-ethylhexyl acrylate (**7e**) resulted in low yield. As observed in catalyst **1**, styrene (**7b**) gave an unsatisfactory result. When the aqueous solution of **Pd-3-N** was reused in the reaction between **6a** and **7a**, the catalyst solution allowed 6 times of reuse and TON reached *ca.* 6000, but it suddenly lost catalytic activity in the seventh use.

Although the reaction proceeded quantitatively with low catalyst loading of 0.05 mol%, the reaction did not proceed at all with 0.03 mol% of the catalyst. Considering the sudden decreased activity at the seventh reuse and the steep deactivation of the catalyst activity upon addition of 0.03 mol% Pd, the possibility of catalyst poisoning was considered. Although the xanthogenate terminus was removed by radical reaction, trace of the sulphur might have remained. A few percent of the sulphur end would be enough to poison the Pd catalyst. Therefore, we carried out the reaction in the absence of **NS** surfactant (Table 1). To our delight, 0.01 mol% of Pd gave the products in moderate to excellent yields for most substrates; even 0.005 mol% Pd afforded the product **8aa** in 90% yield (entry 2). Sterically hindered iodoarenes, again, resulted in low yields (entries 6, 9), although styrene gave the coupling product **8ab** in 34% yield (entry 12).
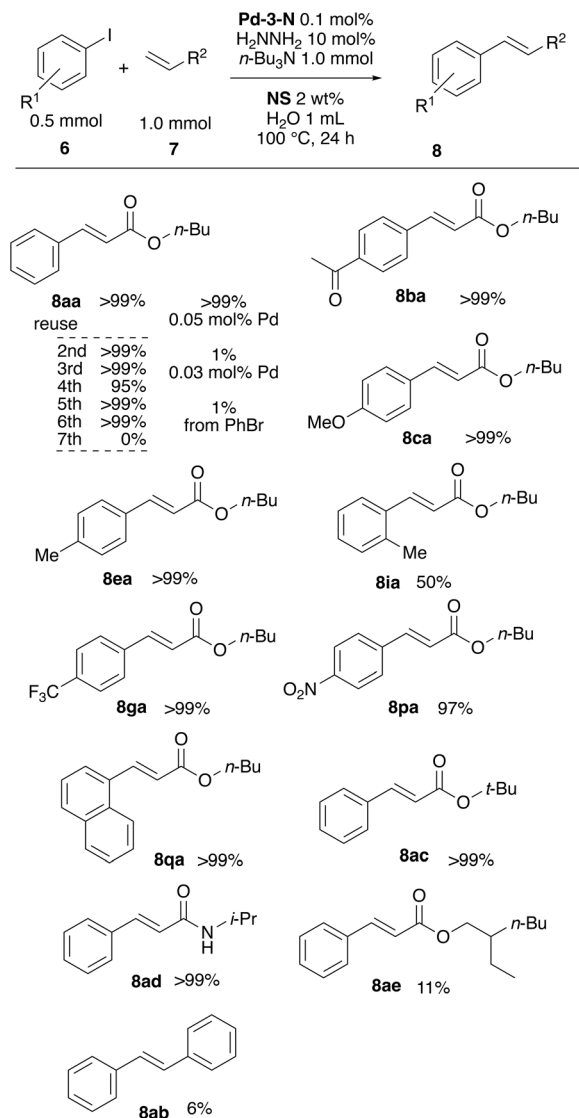
We then studied reuse of the aqueous solution on this system on a larger scale. The reaction was carried out in 10 mL of water in the absence of **NS** using 0.01 mol% of **Pd-3-N** (Fig. 5). The aqueous solution retained its catalytic activity over 8 times of reuse, but the yield decreased to 26% in the ninth use. It should be noted that no extraction solvent was needed to separate the organic layer in this system. Thanks to the larger scale, the organic layer could be separated simply by cooling. Additionally, an organic precipitate was formed, which also contained the product. Both the supernatant and the precipitate were collected, and yields were determined by ¹H NMR. The NMR analyses indicated that 80–90% of the product was contained in the supernatant and that the precipitate consisted of ammonium salts and the remaining product. The recovery was insufficient for the first and second cycles, and the remaining products were recovered after the third and fourth runs. The total turnover number (TON) of the reaction reached 82 800.

3. Experimental

3.1. General

The preparation of RAFT agents and polymers were conducted under an argon atmosphere by using standard Schlenk techniques, unless otherwise mentioned. *N*-Isopropyl acrylamide (NIPAAm) was purchased from Kanto Chemical Co., Inc. and recrystallized from hexane/toluene prior to use. Other chemicals were purchased and used as received. The diblock copolymer **NS** was prepared as previously reported.[63,121–127] Compounds **4, 5** were prepared according to the literature methods.[102,128] Dialysis was performed using Spectra/Por® RC tubing (MWCO: 1.0 kD, 3.5 kD). NMR spectra were recorded on JEOL ECA 500 and Bruker Avance III HD400 spectrometers. Quartets in ¹H

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Chart 3 M–H reactions in water using **Pd-3-N** in the presence of **NS**. Conditions: iodoarenes **6** (0.5 mmol), alkenes **7** (1.0 mmol), n-Bu$_3$N (1.5 mmol), **Pd-3-N** (2.9 mg, 0.05 μmol Pd), N$_2$H$_4$·H$_2$O (0.05 mmol), H$_2$O 1 mL, 100 °C, 24 h.

Table 1 M–H reactions with low Pd loading/no surfactants[a]

a: R^2 = COO-n-Bu
b: R^2 = Ph
c: R^2 = COO-t-Bu
d: R^2 = CONH(i-Pr)

Entries	Haloarenes 6	Alkenes 7	Products 8	Yield of 8[b]/%
1	6a	7a	8aa	>99
2	6a	7a	8aa	90[c]
3	6b	7a	8ba	>99[d]
4	6c	7a	8ca	>99
5	6e	7a	8ea	59
6	6i	7a	8ia	13
7	6g	7a	8ga	31
8	6p (Ar = 4-NO$_2$C$_6$H$_4$)	7a	8pa	51
9	6q (Ar = 1-naphthyl)	7a	8qa	17
10	6a	7c	8ac	95
11	6a	7d	8ad	>99
12	6a	7b	8ab	34%

[a] Conditions: iodoarenes **6** (0.5 mmol), alkenes **7** (1.0 mmol), n-Bu$_3$N (1.5 mmol), **Pd-3-N** (0.29 mg, 0.05 μmol Pd), N$_2$H$_4$·H$_2$O (0.05 mmol), H$_2$O 1 mL, 100 °C, 24 h. [b] Determined by ^{1}H NMR. [c] With 0.005 mol% Pd. [d] 8 h.
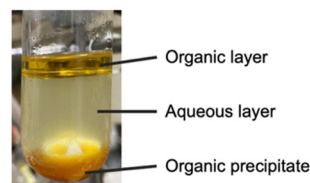
cycle	Yield/%	cycle	Yield/%
1	73	6	106
2	78	7	103
3	125	8	98
4	118	9	26
5	101		

Fig. 5 Reuse of the aqueous solution of **Pd-3-N**.

NMR are denoted by "qt", while quaternary carbons in ^{13}C NMR are denoted by "q". Gel permeation chromatography (GPC) was measured PU-4580 and RI-4030 system (JASCO Corporation) equipped with Shodex GPC KD-802 and KD-803 columns (Showa Denko K.K.) using N,N-dimethylformamide (DMF) (0.1 wt% LiBr) as eluent; the molecular weight of the polymers was determined based on monodispersed poly(ethylene oxide) as standard, and ^{1}H NMR spectroscopy. Scanning transmission electron microscopy (STEM) was recorded on HITACHI Cs-corrected STEM HD-2700 with accelerating voltage of 200 kV, EDX on AMETEK EDAX Octane T Ultra W with 100 mm^2 SDD (Hitachi High-Tech Corporation) measured by CLEARIZE Co. Ltd. and JEM-ARM200F Thermal FE (STEM SDD) at The University of Tokyo.

3.2. Preparation of the RAFT agent bearing N,N-ligand 2

A Schlenk tube was dried, and the azide **4** (381 mg, 1.43 mmol), 2-ethynyl pyridine (147 mg, 1.43 mmol), copper(I) bromide (21 mg, 0.143 mmol), PMDETA (372 mg, 2.15 mmol) were dissolved in DMSO (5.8 mL), and the solution was stirred at r.t. for 4 h. The reaction mixture was extracted twice with ethyl acetate and water, and the organic layer was dried over magnesium sulphate. The desiccant was filtered off, and the filtrate was concentrated *in vacuo* to leave reddish solid. The residual solid was purified by column chromatograph on silica gel (chloroform/hexane = 1/1) to afford the title compound as light-yellow solid (458 mg, 86%). ^{1}H NMR (CDCl$_3$, Me$_4$Si, 500 MHz): δ = 1.41 (t, J = 7 Hz, 3H, CH$_3$), 4.36 (s, 2H, SCH$_2$), 4.65 (qt, J = 7 Hz, 2H, OCH$_2$), 5.56 (s, 2H, NCH$_2$), 7.20–7.23 (m, 1H), 7.28 (d, J = 8 Hz, 2H), 7.37 (d, J = 8 Hz, 2H), 7.77 (td, J = 8, 1 Hz, 1H), 8.04 (s, 1H), 8.17 (d, J = 8 Hz, 1H), 8.54 (d, J = 5 Hz, 1H). ^{13}C{^{1}H} NMR (CDCl$_3$, Me$_4$Si, 125.8 MHz): δ = 13.8 (CH$_3$), 39.8, 54.0, 70.2 (CH$_2$), 120.3, 121.9, 122.9, 128.6, 129.9, 133.7 (q), 136.9 (q), 137.0, 149.4, 150.2 (q), 213.7 (q). High

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resolution MS (ESI): calcd. for $C_{18}H_{18}N_4OS_2$ (M + Na) = 393.0820, found = 393.0809.

3.3. Preparation of PNIPAAm bearing pyridyl triazole end 2-N

Typical procedure for polymerization of N-isopropylacrylamide (NIPAAm) using **2** as a RAFT agent is as follows. A thoroughly dried Schlenk tube (25 mL) was filled with argon. In this vessel, RAFT agent **2** (100 mg, 0.270 mmol), NIPAAm (0.611 g, 5.4 mmol), 2,2′-azobis(isobutyronitrile) (AIBN) (15 mg, 0.09 mmol) were dissolved in dimethylacetamide (DMA) (5 mL) and degassed in three freeze–pump–thaw cycles. The solution was stirred at 60 °C for 24 h, and the mixture was poured into hexane/diethyl ether (300/100 mL). Yellow precipitate was dried in vacuo to afford polymer **2-N′** as pale yellow solid (752 mg, quant.). The polymer was characterized by ^1H NMR spectroscopy to determine polymerization degree (PD = 21, M_n = 2745). GPC M_n = 2578, M_w = 2948, M_w/M_n = 1.14 (based on PEG standard). ^1H NMR (CDCl$_3$, Me$_4$Si, 500 MHz): δ = 4.01 (br, NH), 5.63 (s, 2H, NCH$_2$Ar), 7.77 (s, 1H), 8.03 (s, 1H), 8.16 (s, 1H), 8.53 (s, 1H).

Typically, in a dried Schlenk tube, the polymer **2-N′** (n = 21, 710 mg 0.259 mmol), triethylammonium hypophosphite (376 mg, 1.82 mmol), V-501 (510 mg, 1.82 mmol) were dissolved in DMSO (14 mL).[129] The mixture was degassed by three cycle of freeze–pump–thaw. The mixture was stirred at 80 °C for 5 h. Yellowish solution was dialyzed (MWCO = 1.0 kD), and the solution was dried in vacuo to give **2-N** as white-yellow solid (422 mg, n = 21, 62%). Elemental analysis showed that the amount of sulphur element in **2-N** was less than detection limit. ^1H NMR (CDCl$_3$, Me$_4$Si, 500 MHz): δ = 3.99 (br, NH), 5.54 (s, 2H, NCH$_2$Ar), 7.77 (s, 1H), 8.05 (s, 1H), 8.17 (s, 1H), 8.54 (s, 1H).

3.4. Preparation of polymer-immobilized Pd-complex Pd-2-N

In a dried test tube with a screw cap, the polymer **2-N** (n = 21, 279 mg, 0.106 mmol), PdCl$_2$(cod) (30 mg, 0.106 mmol) were dissolved in acetonitrile (9 mL) and the mixture was stirred at 60 °C for 6 h. The yellow clear solution turned to reddish, and the mixture was poured into hexane/diethyl ether (4/1) to precipitate polymer. Solid was filtered and dried in vacuo to leave dark brown solid (299 mg). The product was identified by ^1H NMR and ICP analysis. ICP analysis showed 3.9 wt% of Pd content, which is consistent with the calculated value (3.8 wt% Pd). ^1H NMR (D$_2$O, Me$_3$Si(CH$_2$)$_3$SO$_3$Na, 500 MHz): δ = 3.89 (br, NH), 5.91 (s, 2H, NCH$_2$Ar), 6.14–8.27 (br, Ar), 9.00 (s, 1H), 9.47 (s, 1H).

3.5. RAFT agent with NNC-pincer ligand 3

The intermediate **11** was synthesized by modified methods of preparation of 2,9-diphenyl-1,10-phenanthlorine.[130,131] The reaction conditions of the cycloaddition reaction were determined with reference to the synthesis method of similar compounds.[132] In a dried Schlenk tube, **11** (0.185 g, 0.52 mmol) and **4** (0.139 g, 0.52 mmol), tris[(1-benzyl-1H-1,2,3-triazol-4-yl) methyl]amine (TBTA) (0.0275 g, 0.052 mmol), sodium L-ascorbate (0.0207 g, 0.104 mmol) were added in ^{t}BuOH (5.3 mL)/H$_2$O (2.7 mL)/CH$_2$Cl$_2$ (3.2 mL). After stirring until the

substrates were dissolved, copper(II) sulphate (82.9 mg, 0.052 mmol) was added and the mixture was stirred at r.t. for 48 h. The solution immediately turned black. After the reaction completed, volatiles were removed in vacuo. Potassium cyanide (329 mg, 5.05 mmol) in water (50 mL) and methanol were added to the residue and sonicated for 1 h. The mixture with light yellow precipitate was concentrated in vacuo to remove volatiles, and the concentrated aqueous mixture was extracted with dichloromethane. The organic layer was washed twice with deionized water and dried over magnesium sulphate. The desiccant was filtered off and the filtrate was concentrated in vacuo. The residue was purified by column chromatograph on silica gel (hexane/ethyl acetate = 1/1) to afford the title compound as yellow solid (281 mg, 87%). ^1H NMR (CDCl$_3$, Me$_4$Si, 500 MHz): δ = 1.42 (t, J = 7.3 Hz, 3H, CH$_3$), 4.38 (s, 2H, CH$_2$S), 4.66 (qt, J = 7.3 Hz, 2H, OCH$_2$), 5.59 (s, 2H, NCH$_2$), 7.29 (d, J = 8.1 Hz, 2H, CH$_2$), 7.40 (d, J = 8.1 Hz, 2H, CH$_2$), 7.50 (t, J = 7.4 Hz, 1H), 7.59 (t, J = 7.5 Hz, 2H), 7.79 (d, J = 6 Hz, 2H), 7.80 (s, 1H), 8.03 (d, J = 8.5 Hz, 2H), 8.17 (t, J = 8.5 Hz, 2H), 8.32 (dd, J = 8.5, 1.1 Hz, 2H), 8.47 (dd, J = 8.1, 1.1 Hz, 2H), 8.53 (d, J = 8.5 Hz, 2H). $^{13}C\{^1H\}$ NMR (CDCl$_3$, Me$_4$Si, 125.8 MHz): δ = 13.8 (CH$_3$), 39.9 (CH$_2$), 53.9 (CH$_2$), 70.3 (CH$_2$), 119.9 (CH ×2), 120.1 (CH), 126.06 (CH), 126.10 (CH ×2), 127.7 (CH ×2), 127.99 (q), 128.03 (q), 128.11 (CH ×2), 128.40 (CH ×2), 128.87 (CH ×2), 129.52 (CH), 129.91 (CH ×2), 131.45 (q), 133.98 (q), 136.87 (q), 136.99 (CH ×2), 139.09 (q), 139.42 (q), 146.07 (q), 146.12 (q), 148.00 (q), 156.12 (q), 156.86 (q), 213.69 (q). High resolution MS (ESI): [M–H] cald for $C_{37}H_{30}N_5OS_2$ = 624.1892, found = 624.1866.

3.6. Preparation of polymer-immobilized Pd-complex Pd-3-N

Polymerization of NIPAAm with **3** is conducted as follows. A Schlenk tube was thoroughly dried and filled with argon. In this tube, **3** (281 mg, 0.45 mmol), N-isopropylacrylamide (NIPAAm) (1.02 g, 9.0 mmol) and azobis(isobutyronitrile) (AIBN) (25 mg, 0.15 mmol) were dissolved in dimethylacetamide (DMA) (9 mL) and degassed by three cycles of freeze–pump–thaw. The solution was stirred at 60 °C for 24 h, and the mixture was poured into hexane/diethyl ether (250/ 100 mL). The yellow precipitate was dissolved in chloroform to recover and the volatile was removed in vacuo to afford **3-N′** as yellow solid (1.203 g, 92%). The polymerization degree was determined by ^1H NMR (n = 45, M_n = 5700). Gel permeation chromatography (GPC) was measured using polyethylene glycol as standard (M_w = 4900, M_w/M_n = 1.23). Removal of the xanthogenate terminus and palladium complexation were conducted similarly to **Pd-2-N**. ICP analysis indicated that Pd content was 1.87 wt% (1.86 wt% calcd.) ^1H NMR (CDCl$_3$, Me$_4$Si, 500 MHz): δ 1.13 (br, CH(CH$_3$)$_2$), 1.64 (br, CH$_2$), 2.15 (br, CH), 3.99 (br, CH–(CH$_3$)$_2$), 7.47–8.50 (m, 16H).

3.7. M–H reactions in water using a polymer surfactant

Typical procedure for M–H reaction in water using the thermo-responsive catalysts in the presence of the thermo-responsive copolymer surfactant **NS** is as follows. In a test

tube with a screw cap, **NS** (40 mg) was dissolved in deionized water (4 mL) and the solution was stirred. To this solution, iodobenzene (**6a**) (102 mg, 0.5 mmol), *n*-butyl acrylate (**7a**) (128 mg, 1.0 mmol), tri-*n*-butylamine (185 mg, 1.0 mmol), catalyst **Pd-2-N** (*e.g.* 22.5 mg, containing 0.005 mmol Pd), hydrazine monohydrate (2.5 mg, 50 μmol) were added, and the mixture was stirred at 70 °C for 48 h. Opaque suspension turned clear by heating, and became reddish solution through the reaction. The reaction mixture was cooled down, and ethyl acetate (0.4 mL) was added and stirred for 5 min and centrifuged. The organic layer was separated and repeated the extraction until the product was not observed by thin layer chromatograph (TLC) in the extract. The combined organic layer was analysed by ^{1}H NMR and gas chromatograph to determine yield of the product **8aa** (92%).

3.8. S–M cross coupling reactions in water using polymer surfactant

Typically, in a test tube with a screw cap, 4-iodoanisole (**6c**) (117 mg, 0.5 mmol) and phenylboronic acid (**9a**) (91 mg, 0.75 mmol), triethylamine (152 mg, 1.5 mmol), **NS** (20 mg) and **Pd-2-N** (*e.g.* 13 mg, containing 0.005 mmol of Pd) were suspended in water (1 mL). The mixture was stirred at 50 °C for 6 h. The reaction mixture was cooled to 0 °C, and then extracted with ethyl acetate (0.2 mL) followed by centrifugation (400*g* for 2 min). The organic layer was analysed by ^{1}H NMR using pyrene as an internal standard. Quantitative formation of **10ca** was observed.

Conclusions

We prepared RAFT agents on which an *N,N*-bidentate ligand was covalently tethered by copper-catalysed Hüisgen cycloaddition. *N*-Isopropylacrylamide was polymerized using these RAFT agents followed by complexation with palladium to afford "thermo-responsive catalysts" whose solubility in water could be switched by temperature. M–H reactions and S–M cross coupling reactions in water using these polymer-tethered catalysts furnished the products in good yields. The thermo-responsive property allowed reuse of the aqueous catalyst solution, which was especially effective for M–H reactions, and a total TON of up to 82 800 was achieved.

Data availability

The data supporting this article have been included as part of the ESI.†

Author contributions

Conceptualization: NS, FYT; formal analysis: NE, RA, CT, YY; funding acquisition: NS, YY; investigation: NE, RA, CT, TYH; project administration: NS, YT, MR: resources: YT, MR, YY; supervision: NS, FYT, YT, MR; validation: CT; visualization: YY; writing – original draft: NS: writing – review & editing: YT, MR.

Conflicts of interest

There are no conflicts to declare.

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