PAPER

Synthesis of new surfactant-like triazine-functionalized ligands for Pd-catalyzed Heck and Sonogashira reactions in water†

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In this study, a novel class of ligands for palladium-catalyzed C–C coupling reactions in water is introduced. A range of triazine-functionalized ligands were synthesized using 2,4,6-trichloro-1,3,5-triazine (TCT) reagent. Among them, N^2,N^4,N^6-tridodecyl-1,3,5-triazine-2,4,6-triamine (**TDTAT**) was found to be an efficient ligand for the Pd-catalyzed Heck and Sonogashira reactions in water, which acted as a green solvent. TEM analysis showed that in the presence of **TDTAT** in water at 80 °C, PdCl₂ is converted to nanoparticles with an average size of ∼3 nm. The formed Pd-nanoparticles act as efficient catalytic species for C–C bond formation reactions in neat water. Under these conditions, Pd-catalyzed Heck and Sonogashira reactions are accomplished without the need for phosphine ligand. The generation of emulsion droplets (5–10 μm) containing Pd(0) nanoparticles would function as an effective reactor to accelerate the rate of the reaction in water media.

Introduction

Transition metal-catalyzed organic transformations are among the most important in organic synthesis.[1] In these reactions, the existence of an appropriate ligand is critical and many of the challenges in this field involve the development of suitable ligands for fine chemical synthesis.[2] Among transition metals, Pd is one of the most efficient ones applied in catalysis, especially in carbon–carbon bond formation reactions.[3] The Heck[4] and Sonogashira[5] reactions are of key significance in synthetic organic chemistry as powerful Pd-catalyzed carbon–carbon bond-forming protocols. Some major problems with these reactions are loss of Pd catalyst in the course of the reaction, high reaction temperature, and the use of phosphine ligands in aprotic and polar solvents such as dimethylformamide (DMF) and dimethylacetamide (DMAc),[6] and these conditions are not consistent with green chemistry principles.[7] In this context, preparation of high performance Pd catalysts and the use of sustainable and environmentally benign reaction conditions have been considered.[8]

Since the main problem is the use of toxic solvents such as DMF for these reactions, several strategies for using water as a solvent have been reported such as the use of water dispersible Pd catalysts,[9] use of solid-support Pd catalysts with hydrophobic surfaces[10] and application of hydrophobic substrates in reaction media such as saccharides.[11] Microemulsions and micellar catalysis are another approach to these reactions in water based on the solubilisation phenomenon.[12,13]

Micellar catalysis is well-known in organic synthesis and has also been used in the Heck reaction.[14] In a micellar catalyst system, an amphiphilic species aggregates in water forming micellar arrangements. The polar portions of the micelle apparently interacts with the surrounding water, and the nonpolar subsection makes up the lipophilic cores to act as hosts for the organic compounds.[15] However, in many of the reported micellar catalyst systems for the Heck and Sonogashira reactions, the existence of a phosphine ligand is necessary, which is not in alignment with green chemistry principles.[16]

2,4,6-Trichloro-1,3,5-triazine (TCT) is an efficient reagent in organic chemistry due its widespread applications.[17] TCT is not only used as a reagent or catalyst in organic synthesis, it is also a base for the synthesis of new materials for other physical and chemical applications.[18] There are some interesting reports in the literature on the use of TCT in the synthesis of ligands for application in metal-catalyzed organic reactions. In fact, to synthesise these ligands, TCT was used as the starting material in order to generate a triazine moiety in the structure of an organic–inorganic hybrid material or polymer.[19]

In the current study, our goal is to develop a novel catalytic system based on TCT and micellar concepts that enable the use of water as a solvent for the Pd-catalyzed coupling reactions. For this purpose, some surfactants were reacted with TCT to generate a set of surfactant-like triazine-functionalized ligands. Thus, in continuation of our previous work on TCT[20] and the design of Pd-catalyst systems for application in cross-coupling reactions under green conditions,[21] we would like to introduce some new and simple surfactant-like triazine-functionalized

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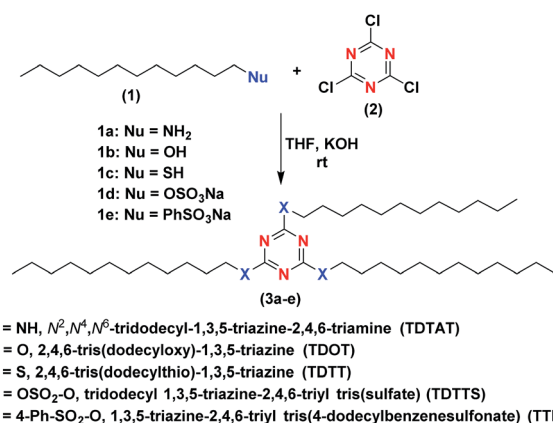† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5ra06753g

ligands for application in the Heck and Sonogashira reactions in neat water.

Results and discussion

Our study was initiated by the synthesis of surfactant-like triazine-functionalized ligands (3a–e) using the reaction of dodecan-1-amine (1a), dodecan-1-ol (1b), dodecane-1-thiol (1c), sodium dodecyl sulfate (SDS) (1d), and sodium 4-dode-cylbenzenesulfonate (1e) with 2,4,6-trichloro-1,3,5-triazine (TCT, 2) (Scheme 1).[22]

The synthetic ligands were characterized using ^{1}H NMR and ^{13}C NMR. These data along with elemental analysis strongly confirm the synthesis of these new ligands (see ESI†).

Next, the synthesized pseudo surfactant triazine-functionalized ligands (3a–d) were used in the Heck reaction

between iodobenzene and styrene in water in order to evaluate their catalytic applicability in this protocol (Table 1).

When **TDTAT** was used as a ligand in the presence of 1.0 mol% of $PdCl_2$ as a pre-catalyst, 74% of the desired product was obtained after 6 h (Table 1, entry 1). By increasing the amount of the Pd to 1.5 mol%, the yield was enhanced to 96% (Table 1, entries 4). The amount of ligand was also changed to an optimum amount of 3.0 wt% (Table 1, entries 4–7). Other synthetic ligands were also tested and among all, **TDTAT** was recognized as the best (Table 1, entries 8–11). These experiments revealed that the type of heteroatom in the surfactant chain is important in the stabilization of Pd species formed during the reaction.

The order of ligand efficiency was found to be **TDTAT** > **TDTT** > **TDOT**, which is in agreement with the ligation power of heteroatoms (NH > S > O) to Pd.[23] The **TDTDS** and **TTDBS** ligands with SO_2 groups did not show good activity in comparison with other ligands, which could well be due to the weak ligation character of the sulfonyl group.[24] This comparison revealed that both the surfactant nature of ligands and ligation character of heteroatoms are important in the activity of this class of ligands.

Subsequently, we checked the effect of other parameters such as the types of base and temperature on the progress of the reaction. The results of these experiments are shown in Table 2.

Some bases, including K_2CO_3, Et_3N, NaOH and Cs_2CO_3, were tested in the model reaction and K_2CO_3 was selected as the best one. Under the base-free conditions, 45% of the product was obtained, demonstrating that the **TDTAT** can act as a weak base in this study. Different temperatures were also checked and 80 °C was selected as the most suitable temperature.

After selection of **TDTAT** as the most efficient ligand in the reaction of the model compound and optimization of reaction conditions, in order to show the merit and applicability of this catalyst system in the Heck reaction, a comparison with other available surfactants was made. The results shown in Table 3 demonstrate the greater efficiency of **TDTAT** in comparison

Scheme 1 Synthesis of surfactant-like triazine-functionalized ligands (3a–e).

3a: X = NH, N^2,N^4,N^6-tridodecyl-1,3,5-triazine-2,4,6-triamine (TDTAT)
3b: X = O, 2,4,6-tris(dodecyloxy)-1,3,5-triazine (TDOT)
3c: X = S, 2,4,6-tris(dodecylthio)-1,3,5-triazine (TDTT)
3d: X = OSO$_2$-O, tridodecyl 1,3,5-triazine-2,4,6-triyl tris(sulfate) (TDTTS)
3e: X = 4-Ph-SO$_2$-O, 1,3,5-triazine-2,4,6-triyl tris(4-dodecylbenzenesulfonate) (TTDBS)

Table 1 The Heck reaction between iodobenzene and styrene in the presence of synthetic surfactant-like triazine-functionalized ligands[a]

Entry	Pd (mol%)	Ligand (wt%)	Time (h)	Yield[b] (%)
1	1.0	**TDTAT** (3)	6	74
2	1.0	**TDTAT** (3)	12	80
3	1.2	**TDTAT** (3)	6	86
4	**1.5**	**TDTAT** (3)	**6**	**96**
5	2.0	**TDTAT** (5)	6	88
6	2.0	**TDTAT** (10)	6	73
7	2.0	**TDTAT** (15)	6	65
8	2.0	**TDOT** (3)	12	75
9	2.0	**TDTT** (3)	12	85
10	2.0	TDTTS (3)	12	63
11	2.0	**TTDBS** (3)	12	60

[a] Reaction conditions: iodobenzene (1 mmol), styrene (1.2 mmol), K_2CO_3 (2 mmol), H_2O (3 mL). [b] Isolated yield.

Table 2 Effect of type of base and temperature on reaction yield

Entry	Base	T (°C)	Time (h)	Yield[a] (%)
1	K_2CO_3	80	6	96
2	Et_3N	80	6	80
3	NaOH	80	6	30
4	Cs_2CO_3	80	6	85
5	No base	80	24	45
6	K_2CO_3	90	6	96
7	K_2CO_3	100	6	95
8	K_2CO_3	rt	24	10
9	K_2CO_3	80	6	96[b]

[a] Isolated yield. [b] 3 mmol of base was used.

Table 3 A comparison of the activities of the **TDTAT** ligand and some other surfactants and chelating substrates

Entry	Surfactant (wt%)	Time (h)	Yield (%)[a]
1	**TDTAT** (3)	6	96
2	Melamine	12	22
3	Dodecyl amine (3)	12	30
4	SDS (3)	12	41
5	TBAB (3)	12	53
6	Triton X-100 (3)	12	60
7	PEG-200 (3)	12	10
8	PEG-200-TCT (3)	12	20

[a] Isolated yield.

with the tested substrates. Melamine and dodecyl amine, fragments of **TDTAT**, were also tested and it was observed that they are not efficient alone. This comparison revealed that the synergistic effect of the triazine ligand could be due to both the pseudo-surfactant character and the good ligation properties of **TDTAT**, which make this compound a very efficient ligand for application in water.

The activity of other surfactants such as SDS, TBAB and Triton X-100 were also evaluated and the obtained results showed that they are not as effective as the **TDTAT** ligand. It should be mentioned that in most of the reports on the use of surfactants in the Heck reaction with water as a solvent, a phosphine or other external ligand has been applied. In continuation of this study, we also checked the effect of PEG-200 on the model reaction but low yield of the product was obtained. Moreover, PEG-200 was reacted with TCT and the synthesized PEG-200-TCT was used instead of **TDTAT** in the reaction but only 20% yield was obtained (Scheme 2). It seems that PEG-200-TCT cannot function in the same manner as other synthetic ligands, because it is different in both the type and length of the chain connected to the triazine moiety. Furthermore, the ratio of the triazine ring to the chain is less, which decreases the ligation role of the triazine rings in the stabilization of Pd species.

These results clearly confirm that the designed surfactant-like triazine-functionalized ligand (**TDTAT**) is much more efficient for the Heck reaction in water.

Consequently, the best conditions for the Heck reaction between iodobenzene and styrene were recognized as shown in Scheme 3.
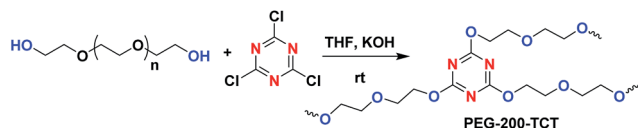
Scheme 2 The synthesis of PEG-200-TCT ligand.
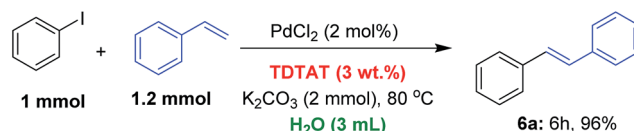
Scheme 3 Optimized conditions for the Heck reaction of iodobenzene and styrene in the presence of the **TDTAT** ligand.

The reaction was also checked with bromobenzene, and after 24 h 80% of the product was obtained. It was observed that at 100 °C the yield of the reaction increased to 89%. Thus, we

Table 4 The Heck reaction of different aryl halides and alkenes under the optimized conditions[a]

[a] Reaction conditions: aryl halides (1.0 mmol), alkene (1.2 mmol), K$_2$CO$_3$ (2.0 mmol), H$_2$O (3.0 mL). Isolated yields are shown.

decided to use 100 °C as the temperature for the Heck reaction of bromoarenes. Chlorobenzene gave the desired product in 60% yield after 48 h at 100 °C, demonstrating that our catalytic system is less efficient for chloroarenes.

The scope of this methodology was evaluated in the Heck reaction for other substrates and the results are depicted in Table 4. As shown in Table 4, this methodology is applicable for different aryl halides with both electron-donating (6b, c, g) and electron-withdrawing groups (6d, e, f, h) in the reaction with styrene. 4-Methyl-5-vinylthiazole was used as another alkene coupling partner in this study and new compounds 6i and 6j were synthesized in good yields. Butyl acrylate was also tested under the optimized conditions with different aryl halides and compounds 6k–r were produced in good to excellent yields, demonstrating that the optimized conditions are also suitable for acrylate substrates. Interestingly, 1-octene also resulted in the corresponding products in good yields (6s–u). These results demonstrate that our strategy is also applicable for un-activated alkene substrates.

We also evaluated the catalytic activity of this catalyst system in the copper-free Sonogashira reaction. Traditionally, the Sonogashira reaction relies on the presence of both palladium and copper to contribute to the catalysis. Much effort of late has

gone into effecting such C–C bond constructions in the absence of cupper. Moreover, while Sonogashira couplings under mixed organic/aqueous conditions are common, reactions in water alone place significant demands on substrate and catalyst solubilities and for this reason they are uncommon. In this paper, we describe a new method that allows Sonogashira couplings to occur in the absence of both copper and organic solvents using commercially available reagents.

Interestingly, the Sonogashira reaction under optimized conditions was accomplished efficiently and the corresponding product was obtained in 92% isolated yield (Scheme 4).
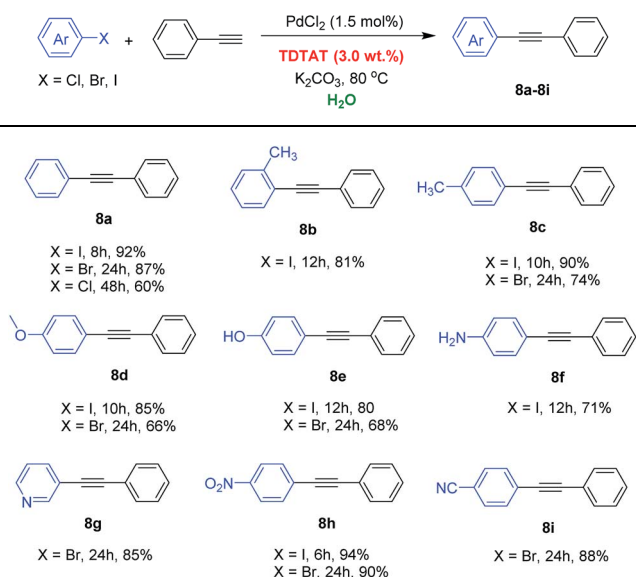
The generality of our method in the Sonogashira reaction between phenylacetylene and different aryl halides was investigated and the corresponding products were obtained in good to excellent yield (Table 5).

As shown in Table 5, aryl halides with electron-donating groups furnished the coupling product in good yield (8b–f). This protocol also worked well when aryl bromides were employed as substrates but with longer reaction time. The possibility of the reactivity of phenol and aniline substrates was also examined and the compounds 8e and 8f were synthesized. A heterocyclic substrate was also checked and the compound 8g was synthesized in moderate yield. The electron-deficient substrates were also suitable in this protocol (8h and 8i).

PdCl$_2$ (1.5 mol%)
TDTAT (3.0 wt.%)
K$_2$CO$_3$, 80 °C
H$_2$O (3.0 mL)

7a   8a: 8h, 92%
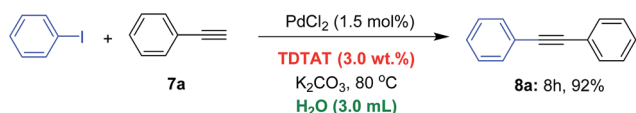
Scheme 4 The Sonogashira reaction between iodobenzene and phenylacetylene using the **TDTAT** ligand under optimized conditions.

Table 5 Products of the Sonogashira reaction using **TDTAT** ligand under the optimized conditions[a]

PdCl$_2$ (1.5 mol%)
TDTAT (3.0 wt.%)
K$_2$CO$_3$, 80 °C
H$_2$O

X = Cl, Br, I   8a-8i

8a
X = I, 8h, 92%
X = Br, 24h, 87%
X = Cl, 48h, 60%

8b
X = I, 12h, 81%

8c
X = I, 10h, 90%
X = Br, 24h, 74%

8d
X = I, 10h, 85%
X = Br, 24h, 66%

8e
X = I, 12h, 80
X = Br, 24h, 68%

8f
X = I, 12h, 71%

8g
X = Br, 24h, 85%

8h
X = I, 6h, 94%
X = Br, 24h, 90%

8i
X = Br, 24h, 88%

[a] Reaction conditions: aryl halides (1.0 mmol), phenylacetylene (1.1 mmol), K$_2$CO$_3$ (2.0 mmol), H$_2$O (3.0 mL). Isolated yields are shown.
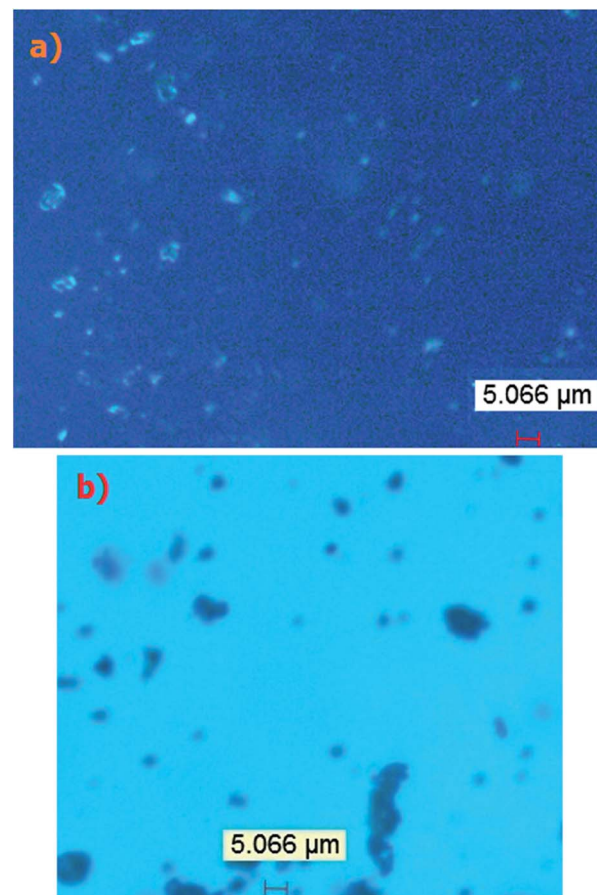

Fig. 1 Optical micrograph of (a) **TDTAT** ligand in water and (b) reaction mixture.

Some other experiments were performed to achieve a deeper insight into the function of this catalyst system. The formation of emulsion droplets in the reaction mixture was confirmed by optical microscopy (Fig. 1). As shown in Fig. 1, formation of emulsion droplets in the micrometer range (∼5–10 μm) was observed for the **TDTAT** ligand in water media. Emulsion droplets were also observed in the reaction mixture. It seems that emulsion droplets containing Pd(0) nanoparticles function as an effective reactor for Pd-catalyzed coupling reactions in water.

We studied the UV spectrum of a mixture of $PdCl_2$/**TDTAT**/H_2O after heating at 80 °C for 6 h. Disappearance of the band around 400 nm was indicative of the absence of Pd(II) under these conditions (Fig. 2). The UV-vis experiment shows that the **TDTAT** ligand can efficiently reduce Pd(II) to Pd(0) under optimized conditions in which it is the reactive species in the Pd-catalyzed process.

The mixture of $PdCl_2$/**TDTAT**/H_2O at 80 °C was analyzed by TEM and the results show that Pd nanoparticles in the average range of 3 nm are produced in the reaction mixture (Fig. 3a). Moreover, the TEM image of the reaction mixture after completion of the reaction shows the existence of Pd nanoparticles in the average range of 15 nm (Fig. 3b). It seems that some particle aggregation occurs while the reaction is progressing.

The catalyst system recyclability of the model reaction was also checked and it was reusable for at least 3 more times (Fig. 4).

The process for the recovery of catalyst is shown in Fig. 5. After completion of the reaction, the product was isolated by decantation and the catalyst was reused for the next run.
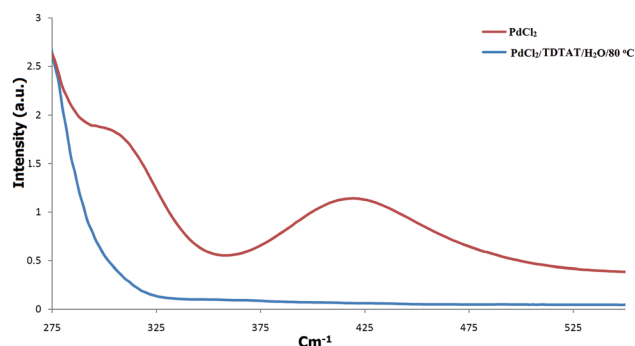

Fig. 2 UV Spectrum of $PdCl_2$ and the mixture of $PdCl_2$/**TDTAT**/H_2O at 80 °C after 1 h.
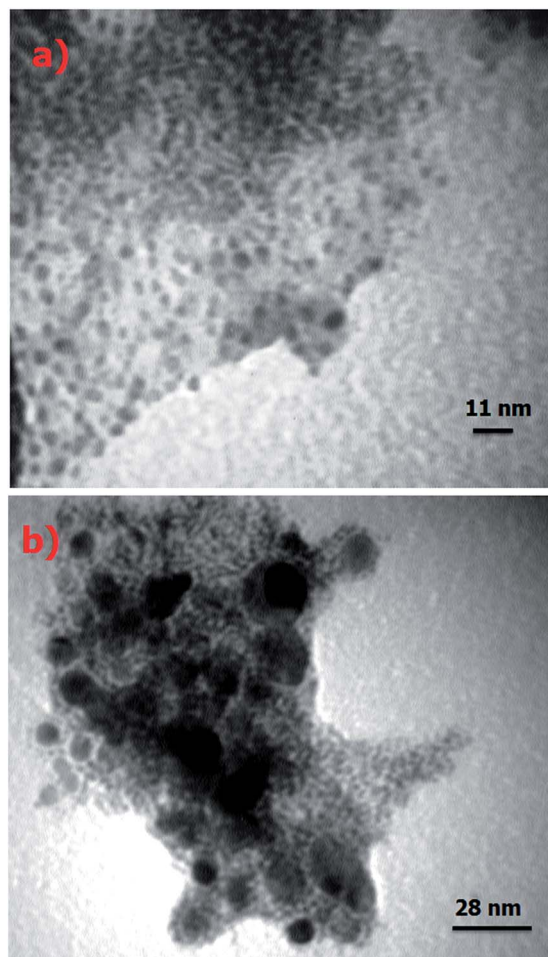

Fig. 4 Reusability of the catalyst system.

Fig. 3 The TEM images of $PdCl_2$/**TDTAT**/H_2O/80 °C before (a) and after reaction (b).
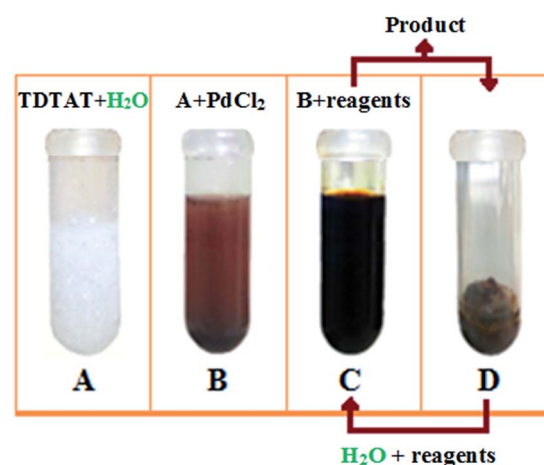

Fig. 5 Recovery of the catalyst system. Image of **TDTAT** in water (A), addition of $PdCl_2$ to the mixture of **TDTAT** and H_2O (B), reaction mixture after completion of the reaction (C), and reused catalyst system (D).

Table 6 Comparison of the results of the synthesis of 1,2-diphenylethene using the TDTAT ligand and other catalyst systems in water

Entry	Catalyst & Conditions	Time (h)	Yield (%)	Ref.
1	PdCl$_2$ (1.5 mol%), **TDTAT** (3 wt%), K$_2$CO$_3$, H$_2$O, 80 °C	6	96	This work
2	PdCl$_2$ (10 mol%), TX10 (10 wt%), PPh$_3$ (0.2 mmol), K$_2$CO$_3$, H$_2$O, 80 °C	6	97	16a
3	PdCl$_2$ (1.0 mol%), CTAB (50 mol%), NaHCO$_3$, H$_2$O, 80 °C	3	89	16c
4	Pd/C (0.01 mol), CTAB (0.5 mol), K$_2$CO$_3$, H$_2$O, 80 °C	4	60	6a
5	Pd/C (0.01 mol), BKC (0.5 mol), K$_2$CO$_3$, H$_2$O, 80 °C	4	77	6a
6	Pd(PPh$_3$)$_4$ (1 mol%), SDS (2.2 wt%), hexadecane, Et$_3$N, H$_2$O, 70 °C	24	99	25
7	PdCl$_2$ (0.3 mol%), TX-100, [BMIM]PF$_6$, H$_2$O, Et$_3$N, 100 °C	2	81	12c
8	Pd(OAc)$_2$@PhSiO$_2$ (1.25 wt%), CTAB (3.3 wt%), propanol (6.6 wt%), H$_2$O (89.3 wt%), K$_2$CO$_3$, 80 °C	8	94	26
9	Pd(OAc)$_2$@sol–gel (1.34 mol%), SDS (3.3 wt%), *n*-BuOH (6.6 wt%), H$_2$O (89.3 wt%), K$_2$CO$_3$, 80 °C	4	99	27

Table 7 Comparison with previously reported catalytic systems for the Sonogashira reaction of aryl iodide with phenylacetylene

Entry	Catalyst & conditions	Time (h)	Yield (%)	Ref.
1	PdCl$_2$ (1.5 mol%), **TDTAT** (3 wt%), K$_2$CO$_3$, H$_2$O, 80 °C	8	96	This work
2	Pd(OAc)$_2$ (3 mol%), TBAB (1.0 mol), K$_2$CO$_3$, EtOH, 80 °C	6	90	28
3	Pd/C (0.02 mol), CTAB (0.125 mol), NaOH, H$_2$O, 80 °C	2	98	29
4	Pd(OAc)$_2$ (2 mol%), 2-aminodiphenyl phosphinite (6 mol%), TBAB (15 mol%), NaOH, H$_2$O, rt	3	92	21f
5	Pd/C (20 mol%), TX10 (19.06 wt%), heptane (6.65 wt%), BuOH (18.86 wt%), H$_2$O : PG (55.43 wt%), K$_2$CO$_3$, 70 °C	0.5	100	30

In order to show the merit and the reactivity of the **TDTAT** catalyst system compared to other catalysts, a comparison with some other reported catalysts for the Heck reaction is presented in Table 6. As shown in Table 6, our catalyst system is superior to some of the previously reported catalysts in terms of reaction conditions, reaction time and yield.

The efficiency of our catalyst system was also compared with some of the previously reported methods in the Sonogashira reaction (Table 7).

As shown in Table 7, our catalyst system is also efficient and green in comparison with other previous reports in activity and reaction conditions.

Conclusions

In conclusion, we have introduced a new class of surfactant: nitrogen ligands for application in transition metal-catalyzed organic reactions. The strategy for the synthetic ligands is simple and they can be prepared from inexpensive and available starting materials. In the synthesis of surfactant-like triazine-functionalized ligands, TCT was used to generate a triazine moiety, and dodecyl substrates were used to supply the surfactant part of the designed ligands. The catalytic activity of the synthetic ligands was evaluated in the Pd-catalyzed Heck and Sonogashira reactions in water, and **TDTAT** was recognized as

an efficient ligand without the use of any phosphine. According to the optical and TEM images, it seems that the formation of droplet particles (5–10 μm) containing nano-Pd species (3–5 nm) functions as an efficient reactor for Pd-catalyzed Heck and Sonogashira reactions in water. We anticipate that these new improved triazine-functionalized ligands can be used for the preparation of other transition metal complexes such as Pt, Ru and Rh for specific applications as catalysts in the related catalyzed reactions.

Experimental section

Chemicals were purchased from Merck and Aldrich chemical companies. All the chemicals and solvents were used as received without further purification. For recording ^{1}H NMR and ^{13}C NMR spectra we used a Brucker (250 MHz) Advance DRX and samples were dissolved in pure deuterated DMSO-d$_6$ or CDCl$_3$ with tetramethylsilane (TMS) as an internal standard. FT-IR spectroscopy (Shimadzu FT-IR 8300 spectrophotometer) was employed for characterization of the compounds. Transmission electron microscopy (TEM) was carried out using a TEM apparatus (CM-10-Philips, 100 kV). Melting points were determined in open capillary tubes in Barnstead Electrothermal 9100 BZ circulating oil melting point apparatus. The reactions were monitored by TLC on silica gel PolyGram SILG/UV254 plates.

Synthesis and characterization of ligands

Synthesis of N^2,N^4,N^6-tridodecyl-1,3,5-triazine-2,4,6-triamine (3a). A mixture of dodecan-1-amine (3.1 mmol), TCT (1.0 mmol), and KOH (3.0 mmol) were stirred in THF (10 mL) in a conical flask (50 mL) at room temperature overnight. After completion of the reaction, as indicated by TLC, the mixture was filtered and washed exhaustively with CH_2Cl_2. The solvent was removed under vacuum. Recrystallization from ethanol gave the product. ^1H NMR (250 MHz, $CDCl_3$): δ (ppm) = 0.85–0.88 (m, 9H), 1.25 (brs, 54H), 1.47–1.64 (m, 6H), 3.31–3.43 (m, 6H), 5.39 (t, J = 5.0 Hz, 3H). ^{13}C NMR (62.5 MHz, $CDCl_3$): 14.1, 22.7, 26.8, 29.3, 29.6, 31.9, 40.9, 163.7. Anal. calcd for $C_{39}H_{78}N_6$: C, 74.23; H, 12.46; N, 13.32. Found: C, 74.10; H, 12.41; N, 13.24.

Synthesis of 2,4,6-tris(dodecyloxy)-1,3,5-triazine (3b). The procedure is similar to 3a. ^1H NMR (250 MHz, $CDCl_3$): δ (ppm) = 0.85–0.90 (m, 9H), 1.25 (brs, 54H), 1.72–1.83 (m, 6H), 4.37 (t, J = 7.5 Hz, 6H). ^{13}C NMR (62.5 MHz, $CDCl_3$): 14.1, 22.6, 25.8, 28.6, 29.3, 29.6, 31.9, 68.5, 172.8. Anal. calcd for $C_{39}H_{75}N_3O_3$: C, 73.88; H, 11.92; N, 6.63. Found: C, 73.75; H, 11.81; N, 6.54.

Synthesis of 2,4,6-tris(dodecylthio)-1,3,5-triazine (3c). The procedure is similar to 3a. ^1H NMR (250 MHz, $CDCl_3$): δ (ppm) = 0.84–0.89 (m, 9H), 1.25 (brs, 54H), 1.73–1.82 (m, 6H), 3.07 (t, J = 7.5 Hz, 6H). ^{13}C NMR (62.5 MHz, $CDCl_3$): 14.1, 22.6, 28.6, 29.3, 29.6, 31.8, 33.5, 172.7. Anal. calcd for $C_{39}H_{75}N_3S_3$: C, 68.66; H, 11.08; N, 6.16; S, 14.10. Found: C, 68.60; H, 11.0; N, 6.09; S, 13.97.

Synthesis of tridodecyl 1,3,5-triazine-2,4,6-triyl tris(sulfate) (3d). The procedure is similar to 3a. ^1H NMR (250 MHz, $CDCl_3$): δ (ppm) = 0.85–0.89 (m, 9H), 1.25 (brs, 54H), 1.60–1.71 (m, 6H), 3.75 (t, J = 7.5 Hz, 6H). ^{13}C NMR (62.5 MHz, $CDCl_3$): 14.1, 22.7, 22.9, 25.9, 28.7, 29.3, 29.6, 31.9, 70.2, 174.9. Anal. calcd for $C_{39}H_{75}N_3O_{12}S_3$: C, 53.58; H, 8.65; N, 4.81; S, 11.00. Found: C, 53.50; H, 8.53; N, 4.75; S, 10.90.

Synthesis of 1,3,5-triazine-2,4,6-triyl tris(4-dodecylbenzenesulfonate) (3e). The procedure is similar to 3a. ^1H NMR (250 MHz, $CDCl_3$): δ (ppm) = 0.85–0.88 (m, 9H), 1.25 (brs, 54H), 1.57–1.68 (m, 6H), 2.71–2.76 (t, J = 7.5 Hz, 6H), 7.35 (d, J = 7.5 Hz, 6H), 7.86 (d, J = 7.5 Hz, 6H). ^{13}C NMR (62.5 MHz, $CDCl_3$): 14.1, 22.7, 29.3, 29.7, 30.1, 31.8, 36.8, 129.8, 131.1, 142.4, 142.7, 163.3. Anal. calcd for $C_{57}H_{87}N_3O_9S_3$: C, 64.92; H, 8.32; N, 3.98; S, 9.12. Found: C, 64.85; H, 8.26; N, 3.91; S, 9.03.

General procedure for the Heck reaction using the TDTAT ligand

A reaction tube equipped with a magnetic stirring bar was charged with aryl halide (1.0 mmol), terminal alkene (1.2 mmol), K_2CO_3 (2 mmol), $PdCl_2$ (1.5 mol%) and **TDTAT**/water (3.0 mL, 3 wt% **TDTAT**). The mixture was heated in an oil bath at 80 °C. After completion of the reaction, monitored by GC or TLC, the reaction mixture was cooled down to room temperature. The organic compound was extracted with ethyl acetate (3 × 5 mL) from the aqueous layer and dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuum. The organic mixture was then purified by silica gel column chromatography using n-hexane/ethyl acetate as an eluent to obtain the corresponding pure coupled product. The recovered catalyst was thoroughly washed with ethyl acetate, dried under nitrogen flow, and was subsequently reused.

General procedure for the Sonogashira reaction using the TDTAT ligand

A mixture of aryl halide (1 mmol), terminal alkyne (1.1 mmol), K_2CO_3 (2.0 mmol), $PdCl_2$ (1.5 mol%) and **TDTAT**/water (3.0 mL, 3 wt% **TDTAT**) was added to a conical flask (10 mL) and stirred at 80 °C. The reactions were monitored by TLC. Stirring was continued until the consumption of the starting materials based on reaction time in Table 5. After completion of the reaction, the mixture was cooled down to room temperature. The organic compound was extracted with ethyl acetate (3 × 5 mL) from the aqueous layer and dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuum. The organic mixture was then purified by silica gel column chromatography employing n-hexane/ethyl acetate as the eluent, affording the pure corresponding product. The recovered catalyst was thoroughly washed with ethyl acetate and was dried under nitrogen flow, and was subsequently reused.

General procedure for the large scale Heck reaction using the TDTAT ligand

A reaction tube equipped with a magnetic stirring bar was charged with aryl halide (10.0 mmol), terminal alkene (11.0 mmol), K_2CO_3 (10.0 mmol), $PdCl_2$ (10.0 mol%) and **TDTAT**/water (30 mL, 30 wt% **TDTAT**). The mixture was heated in an oil bath at 80 °C. After completion of the reaction, monitored by GC or TLC analysis, the reaction mixture was cooled down to room temperature. The organic compound was extracted with ethyl acetate from the aqueous layer and dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuum. The organic mixture was then purified by silica gel column chromatography using n-hexane/ethyl acetate as an eluent to obtain the corresponding pure coupled product.

Acknowledgements

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