Sustainable access to π-conjugated molecular building blocks via phosphine-free, ppm palladium level Suzuki-Miyaura reaction in water

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ABSTRACT

The use of water solutions of surfactants as the reaction medium to carry out cross-coupling reactions on water-insoluble materials is a topic of great interest in sustainable chemistry. Reactions are efficient, fast, compatible with mild or no heating, and require lower catalyst loading with respect to homogeneous phase ones performed in organic solvents. The use of supported, cheap, and widely available catalysts within the context of chemistry in water offers additional advantages: ease of removal, recovery, and recycling of the catalyst as well as a further reduction of costs and environmental impact. We here show that in the presence of a suitable surfactant, palladium-on-carbon – one of the simplest and cheapest supported palladium catalysts – is an exceedingly efficient catalyst to attain ligand-free Suzuki-Miyaura coupling of aryls and heteroaryls in water under standard laboratory atmosphere at Pd loading as low as 400 ppm.

1. Introduction

The advent of green chemistry, or sustainable chemistry, represents one of the most relevant developments of the chemical industry in recent decades. Nowadays all chemical processes are finely tuned during the pre-competitive phase to minimize the amount of wastes, reduce the energy consumption, and the resources depletion both in terms of feedstocks and catalysts [1–5]. Unfortunately, even though the advancement towards sustainability is constant, the chemical industry cannot yet compete with biological transformations having essentially no waste, minimal energy intake, and supremely efficient catalysis. Moreover, the widespread use of toxic and often flammable organic solvents contribute at the same time to the hazardousness of chemical transformations and to the production of large volumes of wastes [1,6, 7].

Water is in many ways the perfect solvent to carry out organic reactions. It is available in large quantities, not toxic, not flammable, and can be stored indefinitely without any hazard occurring. Its high thermal capacity and latent heat of evaporation give also advantages in controlling exothermic reactions when upscaling preparations [2,8].

The fact that most organics are hydrophobic severely limits the number of processes compatible with an aqueous environment, but the conventional wisdom that reagents must be dissolved in a common phase to react efficiently is increasingly being challenged. The last 20 years witnessed an impressive number of examples of reactions involving lipophilic species, efficiently and selectively reacting in water as the prevalent solvent, provided that a suitable surfactant is employed [9–13]. Originally limited in scope by characteristically dilute conditions, surfactant-enhanced reactions are positively revolutionizing the way organic chemistry is done, particularly dealing with metal-catalyzed cross-coupling reactions [14–20].

In the early '80 s, synthetic chemists started realizing that association colloids are a simplified analogous of enzymes: reagents can be hosted and selectively localized within an environment with specific polarity, possibly leading to improved yield and selectivity. The selection of the correct surfactant is crucial to the success of the methods, as demonstrated by the remarkable body of work of Prof. Lipshutz and others [21–27]. The field boomed in the last 10 years, with impressive results already thoroughly reviewed and scaling up efforts actively pursued by major chemical companies [8,13,28–33].

In addition to the still very active areas of research dedicated to the development of new designer surfactants and more efficient catalysts specifically designed to perform well under micellar catalysis conditions, researchers are also developing protocols aimed at replacing molecular catalysts with nanostructured and/or supported heterogeneous ones [34–41]. Firstly, a supported catalyst is easier to remove

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Table 1

Results for the test coupling performed between 3-bromobenzonitrile and 1-naphthylboronic acid. Reaction conditions: bromide (1.0 eq.), boronic acid (1.5 eq.), Na_2CO_3 (1.8 eq.), Pd/C (0.5 mol% of Pd), concentration 0.25 M.
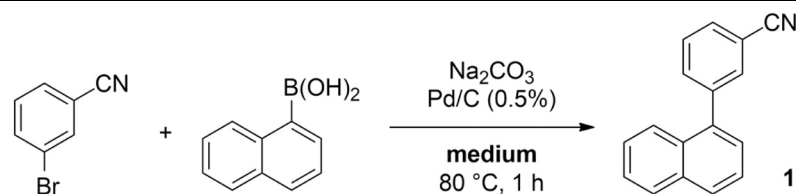
Entry	Medium	Temperature (°C)	Time (h)	Yield (%)
1	iPrOH/H_2O	80	1	100
2	H_2O	80	1	49
2a	H_2O	80	24	58
3	5 wt% Kolliphor EL in H_2O	80	76	1
3a	5 wt% Kolliphor EL in H_2O	80	86	24
3b	5 wt% Kolliphor EL in H_2O	60	86	12
4	5 wt% TPGS-750 M in H_2O	80	24	72
4a	5 wt% TPGS-750 M in H_2O	80	72	87
4b	5 wt% TPGS-750 M in H_2O	60	72	57
5	5 wt% HDAP in H_2O	80	24	no reaction
6	5 wt% Arquad 2HT-75	80	24	no reaction
7	5 wt% ABAC	80	24	no reaction
8	5 wt% Luviquat FC 370	80	24	no reaction
9	5 wt% PAAAC	80	24	no reaction
10	5 wt% CTAB in H_2O	80	1	100
11	5 wt% DTAB in H_2O	80	1	100
12	5 wt% SDS in H_2O	80	1	88
12a	5 wt% SDS in H_2O	80	3	100
13	5 wt% CTAB in H_2O	60	1	100
14[a]	5 wt% DTAB in H_2O	60	3	15
15[a]	5 wt% CTAB in H_2O	60	3	18
16[b]	5 wt% DTAB in H_2O	60	1	100

[a] Catalyst aged for 1 month under laboratory environment
[b] Aged catalyst, hydrogenated for 48 h at 1 bar H_2

from the reaction mixture, which simplifies purification. Moreover, its recycle is also easier with respect to the recovery of molecular catalysts, particularly difficult to disentangle from surfactants during the work up.

Aiming at developing a cheap, simple, and directly scalable strategy to carry out S-M couplings in water and with an heterogeneous catalyst, we focused our attention on the most common commercially available supported palladium species, already having documented applications in this and other palladium mediate couplings: palladium supported on carbon (Pd/C) [42–50]. There are several different grades of this catalyst, varying in terms of the surface area of the carbon support, and the amount and dispersity of palladium on the surface [51]. Literature reports several examples of S-M reactions using different kinds of Pd/C catalysts, commercially available and/or homemade [52,53]. Early reports describe reactions in neat water, performed over water-soluble reagents [54]. In the case of water-insoluble substrates, cationic surfactants can be used for the preparation of various biaryls [55]. Substantial heating and/or microwave activation enable the preparation of more challenging targets [56,57]. Catalyst loading varies depending on the details of the specific reactions, with the lowest documented levels (3000 ppm) reported for reactions in water performed on hydrophilic reagents [58]. Direct comparison between different reactions is somewhat difficult due to the wide availability of different Pd/C catalysts and to the fact that the degree of oxidation of Pd in homemade samples, which clearly impacts on the behavior, is often not discussed [52].

In this study we show that not only S-M couplings are efficient but, once the catalyst is correctly formulated with suitable cationic surfactants, it is possible to push reactions to completion at catalyst loadings as small as 400 ppm, under standard laboratory environment. While optimizing reaction conditions, we became aware of the dynamic nature of this catalyst, observing for the first time that exposure to ambient atmosphere has profound influence on the catalytic efficiency, and impact on aggregation and dispersibility of the catalyst itself. We

developed a formulation chemistry solution to mitigate the problem, dramatically enhancing the shelf life of the catalyst.

We tested the generality of the approach on several aryls and heteroaryls, bearing electron withdrawing and electron donating substituents. Finally, to capitalize on the particularly low metal contamination of our products – a characteristic of interest for molecular semiconductors - we demonstrated the capability to build conjugated Donor-Acceptor luminescent materials characterized by efficient luminescence and high spectral separation between absorption and emission of potential interest for photonic and optoelectronic applications.

2. Results and discussion

For the sake of results standardization, we carried out our study on the commercially available Evonik Noblyst P1092 5 wt% Pd/C, a catalyst known for catalytic hydrogenation reactions, but also suggested by the producer as suitable for C-C couplings. The catalyst is sold as a wet powder to reduce risks associated with pyrophoric behavior, with water content in the order of 40–70 wt%. As the latter varies through the time, we performed a TGA analysis of the powder prior every use to precisely determine the catalyst loading. Another characteristic issue of such catalysis is the copresence of Pd(0) and Pd(II) sites [51,59]. Moreover, the relative abundance of Pd(II) can vary in time due to exposure to ambient atmosphere with extent and kinetics of oxidation depending on the nuclearity of metal clusters. Most synthetic chemists are not particularly aware, nor concerned of such characteristics as Pd/C is generally used under reductive environment (like H_2 atmosphere, phosphines or excess organometallic reagents) where any Pd(II) atom present at the surface would be readily reduced to Pd(0). Interested in developing the simplest possible protocol for S-M coupling in water under heterogeneous catalysis conditions, we firstly tested the commercial Pd/C catalyst working under air and without the use of any
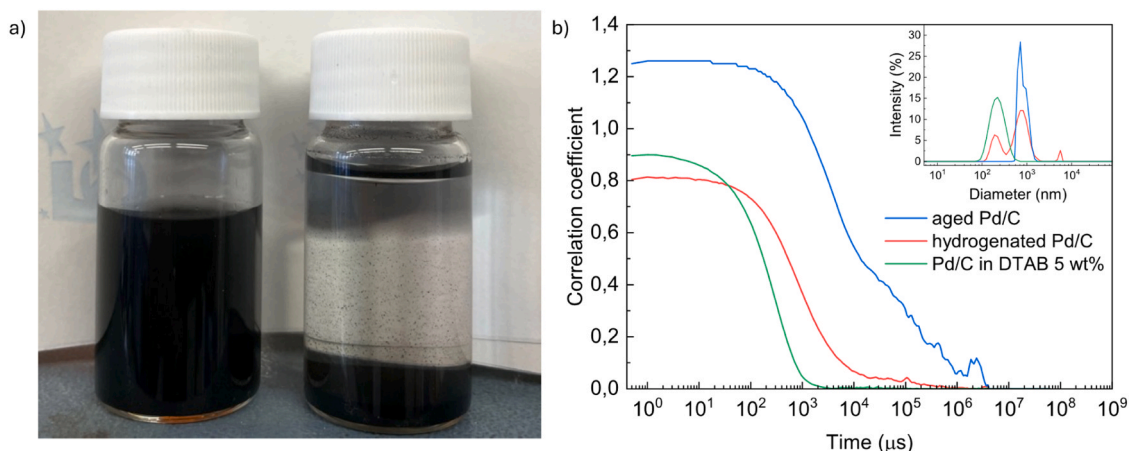
Fig. 1. a) Picture of 2 wt% aged Noblyst P1092 catalyst in deionized water prior (right) and after (left) hydrogenation (48 h, rt, 1 bar) after 24 h from the preparation. b) DLS correlogram of: 1) aged Noblyst P1092 water dispersion (red); 2) hydrogenated Noblyst P1092 water dispersion (blue); 3) aged Noblyst P1092 dispersion in 5 wt% DTAB (green).

phosphine.

Coupling of 3-bromobenzonitrile with 1-naphthylboronic acid (see heading of Table 1) was performed as test reactions. We selected these partners to be able to easily monitor by GC-MS all possible reaction outcomes: the target hetero-coupling derivative **1**, the proto-deborylation product (naphthalene), all the possible homo-coupling derivatives and the dehalogenation side product (benzonitrile). As the baseline for our study, we performed the reaction in a 1:1 vol iPrOH:H$_2$O mixture, capable of fully dissolving the reagents and the base (Na$_2$CO$_3$). We intentionally started with a sizably reduced catalyst loading (5000 ppm) with respect to other literature examples employing this solvent mixtures [60]. We refluxed the reaction under air for 1 h. Entry 1 shows that under such conditions the yield of **1** is quantitative (by GC-MS analysis of the reaction mixture), although sizeable formation of naphthalene and 1,1'-binaphthyl is observed (1-naphthaleneboronic acid is used in excess). It should be noted that the latter is the expected product of Pd(II) promoted reactions, further supporting the presence and impact of such species on the catalyst surface. When carried out in water (entry 2), the reaction is way less performing, displaying a modest 49 % GC-MS yield. Results are quite different from those previously reported for S-M reactions in water using Pd/C as the catalyst, but in our case reagents are not water-soluble [54].

Aiming at a complete removal of organic solvents, we thus tested two nonionic surfactants having particularly remarkable performances in promoting the S-M coupling of a large variety of complex aryls and heteroaryls, while under micellar catalysis conditions: the industrial surfactant Kolliphor EL (a PEGylated castor oil derivative) [61–64] and TPGS-750 M (possibly the most established designer surfactant so far developed) [21,40,65,66]. Both surfactants improved the behavior with respect to pure water, but failed in outperforming the reaction carried out in iPrOH:H$_2$O (entry 3–4). The use of a 5 wt% surfactant concentration instead of the more common 2 wt% was required to improve conversion. We speculate that at lower surfactant concentration, phase separation of the product leads to segregation of the catalyst, severely slowing down the reaction. Indeed, running the very same reaction at 5 instead of 8 wt% of CTAB leads to nearly doubling of the reaction time. Taking inspiration from the existing literature results on the Pd/C promoted coupling of simple biaryls in water solution of surfactants [67,68] we expanded our investigation to cationic and anionic derivatives, with mixed results. As expected from previous results, both CTAB (entry 10) and the closely related dodecyltrimethylammonium bromide (DTAB, entry 11) gave satisfactory results. The anionic monodisperse sodium dodecylsulfate (SDS, entry 12) also gave high yields, albeit requiring a longer reaction time. All other derivatives (entries 5–9, the full name and chemical structures of all the surfactants are reported in Scheme S1

of the Supporting Information) essentially gave no reaction.

As tetraalkylammonium surfactants like CTAB and DTAB are not completely stable at high temperature under alkaline conditions and both boronic acids and esters are prone to thermally activated proto-deborylation, we tested the effect of the reduction of reaction temperature from 80 to 60 °C (entry 13). In the 1 h timespan we set as the reference, the reaction behavior was identical. We thus performed all subsequent studies at such reduced temperature.

All reactions reported in Table 1 were performed over a two-week period, during which time we used the same batch of Pd/C catalyst without noticing any variation in the behavior. We aged the catalyst for three months, just by keeping it under standard laboratory environment, and then repeated the baseline reaction under the previously optimized conditions. As it is shown in entry 14, we observed a dramatically reduced reactivity with a yield of 15 % after 3 h (to be compared with the 100 % after 1 h we observed in the first experimental campaign). The use of CTAB (entry 15) gave essentially the same result.

Not only the catalyst did not perform as well as during the first experimental series, but we also noticed a reduced dispersibility in plain water. Suspecting that a somehow increased tendency to aggregation was impacting on the availability of the catalytic sites, we premixed both catalyst and surfactant in water observing a gradual improvement in the dispersibility. Over a period of three days, we kept sampling the dispersion repeating the test reaction. We observed a gradual improvement in both the homogeneity of the mixture and in conversion and yield of the reaction. After 3 days, we restored the fresh catalyst performances. From then on, the dispersion could be used for days without noticing any further evolution in the behavior.

As mentioned in the introduction, we did not expect the Pd/C catalyst to be indefinitely air stable. Over time, the most exposed Pd(0) sites might oxidize to Pd(II), thus reducing the effective catalyst loading. This effect alone explains the reduction over time of the catalytic efficiency but does not directly explain the role of the surfactant in restoring the original performances. Also, literature shows that the presence of Pd(II) sites per se does not prevent efficient S-M coupling, provided that an excess of boronic acid is employed [46,47]. The formation of heavy divalent cations such as Pd(II) does not exclusively impact on catalysis but on the formulative stability of the heterogeneous reaction mixture as well. Indeed, it is known that multivalent cations can trigger the coagulation of waterborne dispersions, above a characteristic concentration known as the Critical Coagulation Concentration (CCC) [69,70]. Above CCC a normally easily water dispersible solid, forms aggregates and readily flocculates. The addition of a dispersant counterbalances the effect of the electrolyte and restores dispersibility. To prove the impact on dispersibility of the formation of Pd(II) species on carbon surface, we

Table 2

Optimization of reaction conditions for the test coupling reaction performed between 3-bromobenzonitrile and 1-naphthylboronic acid. Reaction conditions: bromide (1.0 eq.), boronic acid (1.5 eq.), base (1.8 eq.), Pd/C concentration 0.25 M, temperature 60 °C.
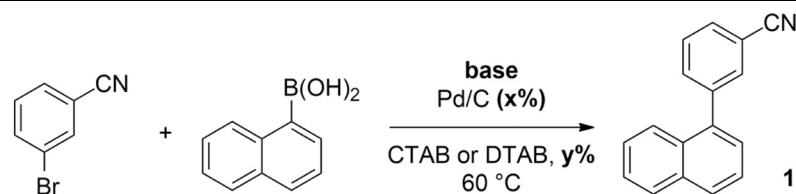
Entry	Base	[Pd] (ppm)	Surfactant	Time	Yield (%)	TON
1	Na$_2$CO$_3$	5000	5 % CTAB	1 h	100	340
2	Na$_2$CO$_3$	1000	5 % CTAB	1 h	100	1700
3	Na$_2$CO$_3$	400	5 % CTAB	1 (3) h	41 (67)	1743 (2848)
4	Et$_3$N	400	5 % CTAB	3 h	60	2550
5	K$_3$PO$_4$	400	5 % CTAB	3 h	75	3188
6	K$_3$PO$_4$	400	8 % CTAB	1 h	100	4250
7	K$_3$PO$_4$	40	8 % CTAB	120 h	50	21250
8	K$_3$PO$_4$	-	8 % CTAB	120 h	nr	-
9	K$_3$PO$_4$	400	5 % DTAB	3 (6) h	95 (100)	4038
10[a]	K$_3$PO$_4$	400	5 % DTAB	3 h	100	4250

[a] Reaction performed at 0.5 M concentration.

hydrogenated a sample of the aged Noblyst P1092 catalyst (1 bar, rt, 48 h) and we compared its dispersibility in water with respect to the aged sample. As it is shown in Fig. 1a, the stability of the two 2 wt% water dispersions after 24 h was completely different. The aged catalyst completely settled, conversely the hydrogenated sample gave a stable dispersion, even in the absence of a dispersant.

Fig. 1b shows a comparison between the DLS correlograms of the aged (blue), hydrogenated (red) and DTAB treated aged catalyst (green) in water. The two correlograms pertaining to the hydrogenated and DTAB treated samples are similar and show a nearly ideal curve, hinting at a stable and homogeneous suspension. The inset report the intensity plot for the same measurement showing that the DTAB sample consists of particles having a monomodal distribution centered at around 300 nm. The hydrogenated sample shows the same kind of primary particles, alongside with bigger secondary aggregated particles. The aged catalyst trace shows a very broad and irregular correlogram, associated with particles above the 1 μm threshold.

Not only the hydrogenation restores the original dispersibility in water of the Noblyst P1092 catalyst, but it also restores the original reactivity without any need of premixing and aging in the surfactant solution (Entry 16, Table 1).

A clear-cut interpretation of our results based on the indications at hand is not possible, even though our data constitute circumstantial evidence for the following model. The as prepared catalyst is dispersible and efficient. As soon as a sufficient number of the Pd(0) sites are oxidized to Pd(II), coagulation proceeds, leading to larger particles that cannot be redispersed in water without the aid of a surfactant. As a minimal amount of water wets the Pd/C, even at very moderate oxidation level the concentration of the Pd(II) ions can easily reach the typical CCC values expected for divalent cations on carbonaceous nanomaterials (in the order of 0.01 M). From the moment the coagulation occurs, any further oxidation is hindered by the tightly packed nature of the aggregates. Carrying out a reaction on such a materials leads to poor results due both to unfavorable surface to volume ratios and unavailability of the Pd(0) catalytic sites. The aging in the surfactant solution disaggregates the coagulates, thus making all the catalytic sites available. As most of the Pd(0) sites are protected by the coagulation, the redispersed catalyst recovers its original efficacy. Hydrogenation of the aged and coagulated catalyst restores both dispersibility and catalytic activity due to the reduction of Pd(II) species. According to our experience, the best way to implement Pd/C in S-M reactions performed in air and under phosphine-free conditions is the pretreatment of the

coagulated (and thus preserved) powder with the 5 wt% DTAB solution. In this way the variability in the catalyst behavior due to the evolving Pd(0)/Pd(II) ratio is effectively removed and the catalytic efficiency is preserved.

Having sorted out the aging/reproducibility issue, we further optimized conditions aiming at finding out the limiting Pd loading, while keeping the reaction time short enough to minimize side reactions (Table 2).

Reduction of the palladium loading to 1000 (Entry 2) does not impact on the reaction behavior. Thus, we further reduced it to 400 ppm (entry 3), a state-of-the-art palladium loading for S-M reactions, even when working with specialized phosphines [71–75]. The reaction remains somewhat performing even if the yield after 1 h is reduced at 41 %, reaching 67 % after 3 h. We noticed that, while working at such a low catalyst level, the reaction mixture did not look homogeneous, with the catalyst accumulating in some portions of the dispersion. We thus tested the use of an organic base (NEt$_3$) to improve the formulative state by acting as an organic cosolvent, but the yield remained limited to 60 % after 3 h (entry 4). The switching to the stronger base K$_3$PO$_4$ instead allowed to further raise the conversion to 75 % in 3 h (entry 5). We also observed that the accumulation of the product triggered the phase separation of the catalyst, becoming clearly visible as micrometric dark grains. The effect can be counterbalanced by the raising the CTAB concentration from 5 to 8 wt%, resulting in a much more homogeneous dispersion of reagents and products, thus making the (very few, at this catalyst loading) catalytic sites available for further reaction. At 400 ppm of Pd and with 8 wt% of CTAB, the reaction is quantitative after only 1 h (entry 6). Aiming at pushing the reaction to the limit, we tested a 40 ppm catalyst loading. To do so, we had to perform the reaction using 36 g (0.2 mol) of 2-bromobenzonitrile just to be able to reliably weight the amount of Pd/C (2 mg of 50 wt% hydrated sample). As expected, the reaction became significantly slower, to the point that the hydrolysis of the nitrile becomes a competitive process, thus making the monitoring more complex. After 120 h, we isolated the product in 50 % yield with a very remarkable 21250 TON (entry 7). The use of such a small amount of catalyst loading might not seem worth the effort, particularly because of the increased reaction time and decreased conversion (mostly due to concomitant protodeborylation). Resources depletion alone does not justify the effort as 400 ppm already is a very small amount of catalyst. The main reason why heterogenous catalysis is considered attractive over homogeneous one is the recovery of the catalyst. While working at such a small catalyst loading, recovery and
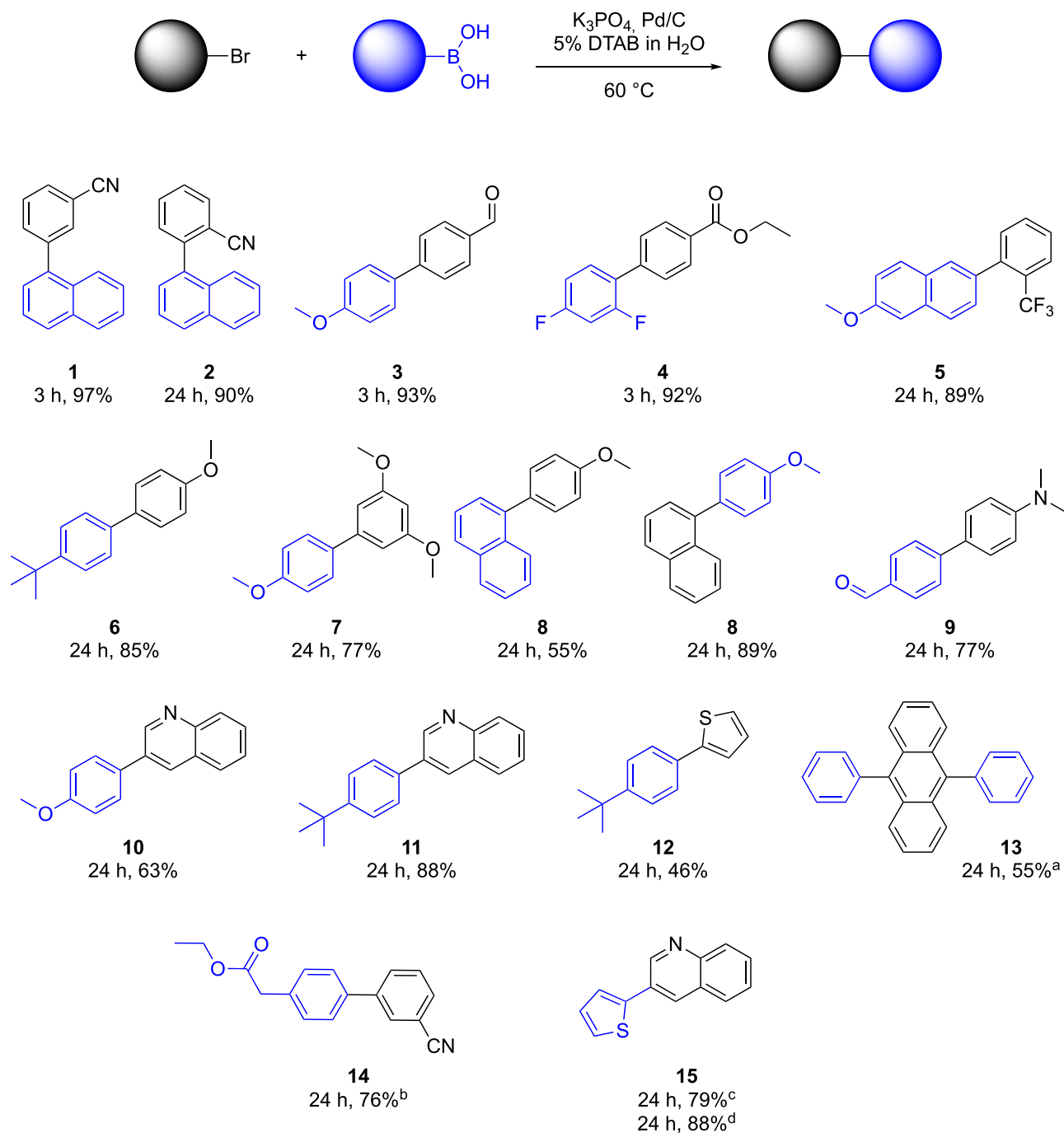
Scheme 1. Coupling products obtained using optimized Suzuki-Miyaura conditions at 400 ppm catalyst loading. Exception to the general protocol: a) reaction was performed at 70 °C; b) reaction preformed with the pinacol ester of the corresponding boronic acid; c) Catalyst loading 35000 ppm; d) catalyst loading 2000 ppm, reaction performed under nitrogen and in the presence of 4000 ppm of X-Phos.

recycle might be challenging as the typical reaction contains less than 1 mg of palladium for mmol of reagents. The contamination of the product is much more relevant. At the optimized palladium loading of 400 ppm, ICP-MS detected less that 2 ppm Pd contamination in the purified product. This value is well below the 10 ppm level admitted for oral drugs [76]. While working at 50 ppm level, the concentration of Pd in the purified product was below the instrument sensitivity.

As expected, the complete removal of the catalyst gives no reaction at all (entry 8). Working at 8 wt% surfactant concentration makes isolation of the product tedious, especially because CTAB is poorly soluble in water at room temperature. The replacement with DTAB, its water-soluble counterpart at r.t., enables keeping molar concentration similar while working at the more manageable 5 wt% concentration. Entry 9 shows that the replacement does not impact on the yield but makes the reaction slower. This is likely due to partial phase segregating of the catalyst at high conversions. Instead of raising again the surfactant concentration, we raised the concentration of the bromide from 0.25 M to 0.50 M, achieving quantitative yield in 3 h.

To further explore the scope and generality of the method, we selected a set of bromides and boronic acids featuring aromatics bearing electron withdrawing and donating substituents as well as hetero-aromatics, both π-deficient and π-excessive. This peculiar selection was due to our focus in the development of building blocks useful for the preparation of polyconjugated derivatives of interest for printed
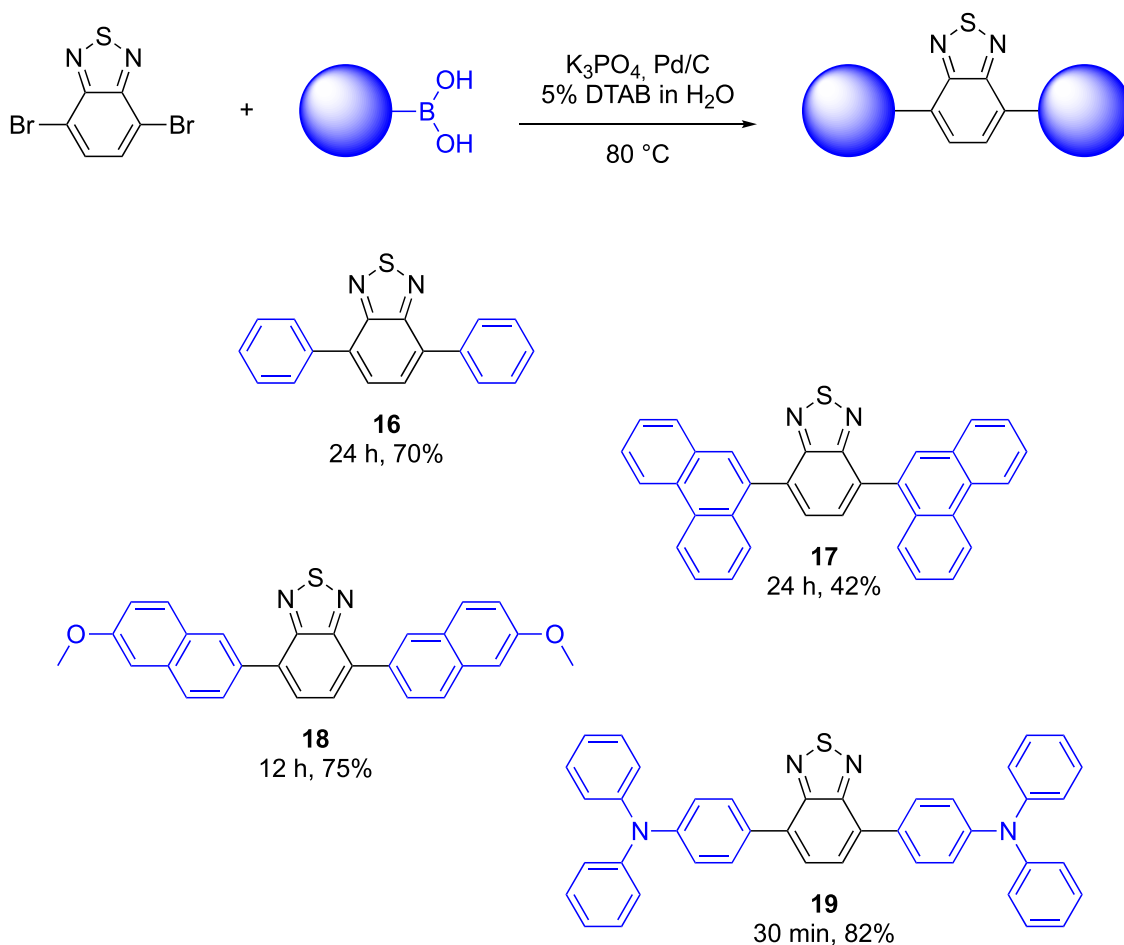
Scheme 2. 4,7-diarylbenzothiazole derivatives with extended conjugation synthesized via phosphine-free, Suzuki-Miyaura optimized protocol in water at 1000 ppm catalyst loading.

electronics, a technological area at the verge of the Lab to Fab transition and consequently in great need of green chemistry compliant manufacturing protocols[77]. Scheme 1 summarizes the obtained results.

The behavior of all reactions is in line with the reactivity generally observed in S-M reactions carried out under homogeneous conditions. Coupling on unhindered electron-poor bromides is generally fast and efficient, reaching complete conversion in 3 hours at isolated yields above 90 % (derivatives **1**, **3** and **4**). The reaction slows down when leading to the formation of a sterically hindered product (derivative **2** and **5**). Electron-rich bromides also require longer reaction times and generally give poorer results (derivatives **6-9**). The tolerance of functional groups is in line with the behavior of standard S-M, giving good results with aldehydes as well as with hydrolysable groups (derivatives **3** and **4**). Heteroaryl species also give satisfactory yields, only requiring prolonged reaction times. We observed complete conversion for the coupling of 2-bromothiophene with 4-tertbutylphenylboronic (derivative **12**) and 3-bromoquinoline with 4-anisylboronic acid (derivative **10**). Finally, we prepared the well-known fluorescent standard, 9,10-diphenylanthracene **13**. In the past we successfully prepared **13** and other 9,10-diarylanthracene derivatives under micellar catalysis conditions, using the rather expensive Pd(dtbpf)Cl$_2$ molecular catalyst at 3 mol% loading [61]. Performing the reaction with 800 ppm Pd/C (400 ppm for every bromide equivalent) at 70 °C for 24 h gave **12** in 55 % isolated yield, to be compared with the 25 % (at 30,000 ppm level!) we previously obtained. Interestingly, the reaction mixture is homogeneous only up to 70 °C, above such temperature we observed massive phase separation. We prepared **14** starting from a boropinacolate ester instead of a boronic acid to test the robustness of the method toward the boron containing precursor and we observed a comparable behavior. Derivative **15** shows that the protocol works poorly with thiophene containing boronic acids, combining reduced reactivity and high tendency to protodeborylation. Indeed, in this case the conversion while working at 400 ppm catalyst loading was negligible. To obtain a 79 % yield we had to raise it up to 35000 ppm (3.5 mol%), a value that could be reduced to 2000 ppm only working under N$_2$ atmosphere and in the presence of X-Phos (the structure of the X-Phos phosphine is reported in Figure S1 of the Supporting Information).

Intrigued by the particularly good performances we obtained with extended conjugation materials like **13**, we synthetized a series of 4,7-diarylbenzothiazole derivatives bearing lateral groups having further increased π-conjugation. The use of phenylboronic acid gave **16** in 70 % yield, to be compared with the 96 % we obtained with Pd(dtbpf)Cl$_2$ (still at 30000 ppm). All other derivatives gave comparable results (75 % yield for the naphthalene end capped **18** and 82 % yield for the triphenylamine end capped **19**). Only the sterically hindered phenanthrene functionalized **17** was isolated in a more modest 42 % yield. Scheme 2.

Fig. 2 shows the normalized absorption and emission spectra of derivatives **16-19**, highlighting the particularly large Stokes Shift – typical of strongly conjugated Donor-Acceptor-Donor compounds – as well as the increasing donating capabilities of the phenyl<phenantryl<6-methoxynaphtyl<triphenylamino end capping units.
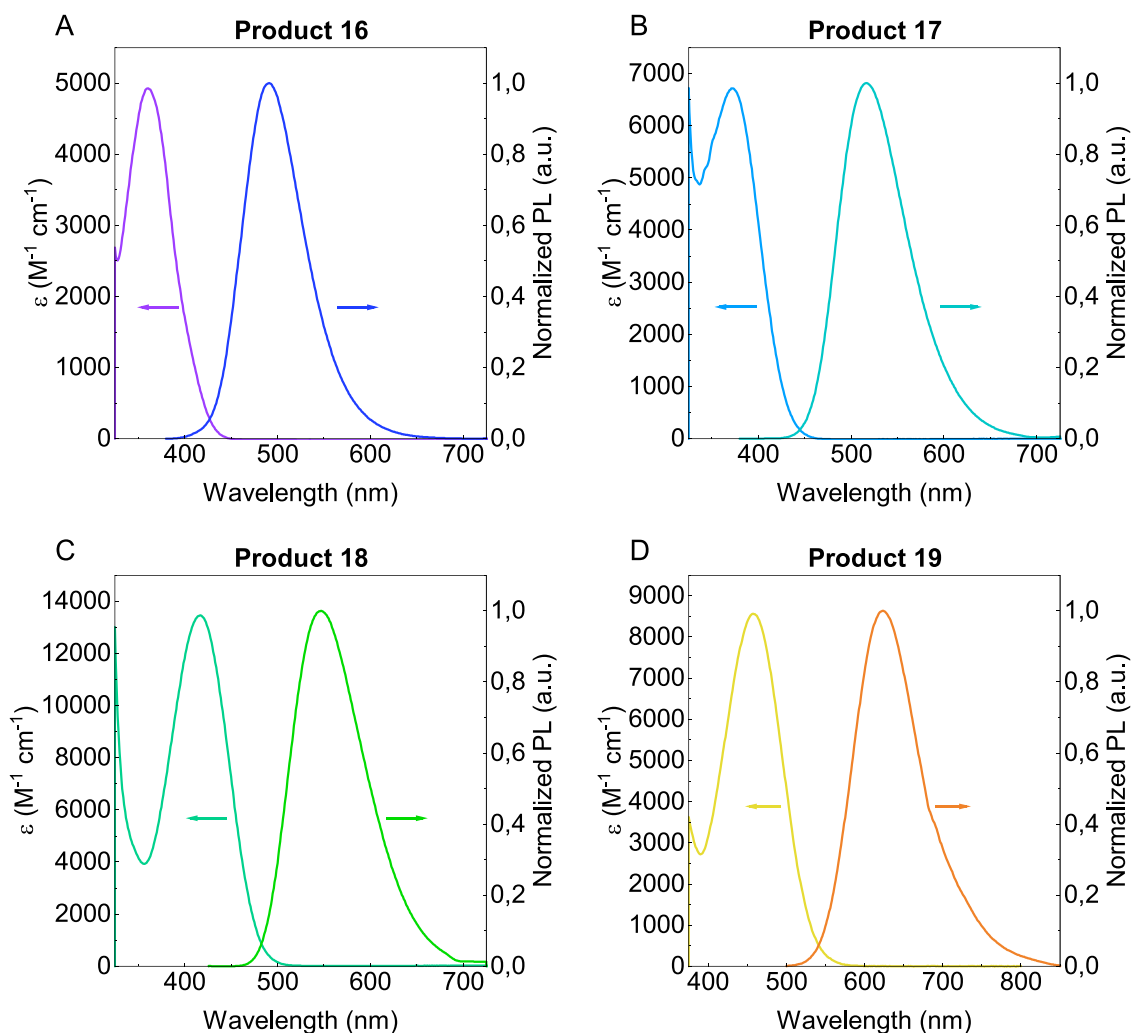
Fig. 2. UV-Vis absorption and normalized emission spectra of CH$_2$Cl$_2$ solutions of derivatives **16–19**.

3. Conclusions

We have demonstrated that, in the presence of the industrial cationic surfactants CTAB and DTAB, palladiated carbon is an exceedingly efficient heterogeneous catalyst for the Suzuki-Miyaura coupling of a variety of substituted aryls and heteroaryls in water, in high yield, under standard laboratory atmosphere and in the absence of a phosphine ligand. The method can be profitably applied to the synthesis of various building blocks of conjugated materials for optoelectronic applications. We also observed, to the best of our knowledge and for the first time, that Pd/C dispersibility in water under laboratory environment evolves during time, alongside with a progressive decrease in catalytic activity. We offered circumstantial evidences that such behavior is connected with the accumulation of Pd(II) ions, progressively leading to coagulation. We showed that this process is reversible, as hydrogenation of a water dispersion of aged catalyst restores both catalytic activity and dispersibility. Even more importantly, the same result can be obtained without recurring to the use of potentially harmful gaseous reducing species, simply by ripening the aged catalyst in a water solution of cationic surfactant. The progressive dispersion of the coagulated catalyst particles exposed new Pd(0) sites, thus recovering the original reactivity. Finally, we demonstrated the possibility to conduct efficient S-M couplings with both hydrogenated and surfactants processed Pd/C catalysts, at the unprecedently low catalyst loading of 400 Pd ppm.

CRediT authorship contribution statement

Luca Beverina: Writing – review & editing, Writing – original draft, Conceptualization. **Mauro Sassi:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Data curation. **Erika Ghiglietti:** Investigation. **Sara Mattiello:** Writing – original draft, Supervision, Methodology, Formal analysis, Data curation. **Nicolò Giulini:** Investigation. **Miriam Ciallella:** Investigation. **Annapia Fratepietro:** Investigation. **Alice Fappani:** Investigation.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Luca Beverina reports financial support was provided by MUR. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.cattod.2024.114893.

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