Palladium–poly(ionic liquid) membranes for permselective sonochemical flow catalysis

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ABSTRACT

Anisotropic palladium–poly(ionic liquid) catalyst membranes have been prepared by complexation of palladium (II) chloride to poly(ionic liquid) functionalised flexible porous substrates. The practical viability of these low loading (sub 0.1 mol%) palladium catalyst membranes for continuous flow reactions at ambient temperature is demonstrated for the Suzuki–Miyaura carbon–carbon coupling reaction by contacting the reactant mixture with the catalyst membrane and applying sonication. The Suzuki–Miyaura carbon–carbon coupling reaction proceeds at the palladium–poly(ionic liquid) catalyst membrane surface in conjunction with selective permeation (separation) of the desired product species through the underlying porous support. These palladium–poly(ionic liquid) catalyst membranes display minimal metal leaching enabling them to be reused multiple times.

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1. Introduction

Ionic liquids are used for a wide range of applications including catalysis [1–3]. In the case of the Suzuki–Miyaura carbon–carbon coupling reaction, palladium species immobilised within ionic liquids have been shown to be highly effective catalyst systems [4–16]. For instance, ionic liquid imidazolium cations can coordinate palladium catalyst centres [4–15]. The covalent attachment of ionic liquids to conventional polymer backbones such as poly(vinylbenzyl) [7,12] and poly(divinylbenzene) [13] has also been reported [17]. Whilst such systems can produce high yields and reaction selectivities [4–16], the inherent requirement for elution of the product limits their more widespread application. Other disadvantages include the need for high metal catalyst loadings, metal loss due to leaching, or catalyst breakdown; all of which can lead to additional processing steps and extra costs being incurred (e.g. post-reaction metal recovery in order to comply with public health regulations for pharmaceutical active ingredients [18]).

For the case of heterogeneous catalyst Suzuki–Miyaura carbon–carbon coupling reaction systems, palladium dispersed onto carbon (Pd/C) provides ease of product recovery, a relatively high reaction rate, lower cost, and integration into packed bed reactors or columns [19–22]. However, not only are high temperatures and loadings necessary to achieve adequate yields, significant levels of metal leaching are observed. Lower palladium loadings have been reported for other solid support materials (these include metal phosphates [23], metal oxides [24], and organic polymers [25]). Despite such heterogeneous systems displaying reduced palladium leaching compared to conventional Pd/C systems, elevated temperatures or microwave heating are still needed to achieve high product yields. Microchannel and capillary reactors are alternatives to packed bed reactor systems, benefiting from lower loadings, high turnover frequencies (TOFs), and low levels of catalyst leaching [26,27]. Their drawback is the small active catalytic areas available in such devices limiting the overall reaction product capacity compared to conventional larger-scale packed bed flow reactors.

Hybrid catalyst–membrane systems can potentially address the aforementioned limitations. Poly(ionic liquids) supported onto membranes have been prepared by photo-initiated grafting of imidazolium groups onto polyethersulfone membranes [28]. The resulting membrane supported palladium–poly(ionic liquid) catalysts yield rapid TOFs (174 h$^{-1}$, moles of product per mole of palladium per hour), but operate at above ambient temperatures (333 K).

In this article, we describe a continuous flow anisotropic palladium–poly(ionic liquid) catalyst membrane system containing the above advantages of low Pd loading, but which operates at low temperatures (293 K) and delivers comparable performance (TOF = 154 h$^{-1}$). Its fabrication comprises pulsed plasma deposition of a poly(vinylbenzyl chloride) layer onto a membrane to generate surface benzyl chloride groups followed by the Mensutkin reaction to form surface tethered quaternised N-butylimidazole moieties which are subsequently used to complex palladium chloride catalyst to the imidazolium cations [29], Scheme 1.

The pulsed plasma deposition step entails modulating an electrical discharge in the presence of vinylbenzyl chloride gaseous precursor containing a polymerisable carbon–carbon double bond [30,31]. Mechanistically, there are two distinct reaction regimes corresponding to the plasma duty cycle on- and off-periods (typical timescales are of the order of microseconds and milliseconds respectively) [32]. Namely, monomer activation and reactive site generation occur at the substrate surface during each short burst of plasma (via VUV irradiation, ion, or electron bombardment) followed by conventional carbon–carbon double bond polymerization proceeding in the subsequent extended off-period (in the absence of any VUV-, ion-, or electron-induced damage to the growing film). High levels of precursor functional group structural retention within pulsed plasma deposited nanolayers can be achieved (as confirmed by ToF-SIMS [33] and NMR [34]). Furthermore, by programming the pulsed plasma duty cycle, it is possible to control (i.e. tailor) the surface density of desired chemical groups. Strong covalent attachment of the deposited functional layers to the underlying substrate occurs via free radical sites created at the interface during the onset of plasma exposure (this has allowed for the preparation of flexible substrate heterogeneous catalyst systems [35]). Other distinct advantages include the fact that the plasmachemical approach is quick (single-step), solventless, energy-efficient, and the reactive gaseous nature of the electrical discharge provides conformality to the host substrate membrane material [36,37].

The palladium–poly(ionic liquid) catalyst membranes fabricated in
the present study have been employed for the Suzuki–Miyaura carbon–carbon coupling reaction, Scheme 2.

2. Experimental

2.1. Preparation of palladium–poly(ionic liquid) catalyst membrane

A cylindrical glass reactor (5.5 cm diameter, 475 cm³ volume) housed within a Faraday cage was used for plasmaschemical deposition. This was connected to a 30 L min⁻¹ rotary pump (model E2M2, Edwards Vacuum Ltd.) via a liquid nitrogen cold trap (base pressure less than 2 × 10⁻³ mbar and air leak rate better than 6 × 10⁻⁹ mol s⁻¹) [38]. A copper coil wound around the reactor (4 mm diameter, 10 turns, located 10 cm downstream from the gas inlet) was connected to a 13.56 MHz radio frequency (RF) power supply via an L–C matching network. A signal generator (model TG503, Thurlby Thandar Instruments Ltd.) was used to trigger the RF power supply. Prior to film deposition, the whole apparatus was thoroughly scrubbed using detergent and hot water, rinsed with propan-2-ol (+99.5 wt.%, Fisher Scientific UK Ltd.), oven dried at 423 K, and further cleaned using a 50 W continuous wave air plasma at 0.2 mbar for 30 min. Silicon substrate preparation comprised successive sonications in propan-2-ol and cyclohexane (+99.7 wt.%, Sigma–Aldrich Co.) for 15 min prior to insertion into the centre of the chamber. Further cleaning entailed running a 50 W continuous wave air plasma at 0.2 mbar for 30 min prior to film deposition. Polytetrafluoroethylene (PTFE) film (180 ± 10 μm thickness, 5 ± 2 μm surface pore size determined by SEM, Mupor Ltd.) was used following rinsing in a 1 : 1 vol. ratio mixture of cyclohexane and propan-2-ol. Vinylbenzyl chloride (mixture of 3- and 4-isomers, 97 wt.%, Sigma–Aldrich Co.) precursor was loaded into a sealable glass tube, degassed via several freeze–pump–thaw cycles, and then attached to the reactor. Monomer vapour was then allowed to purge the apparatus at a pressure of 0.15 mbar for 15 min prior to electrical discharge ignition. Pulsed plasma deposition was performed at 293 K using a duty cycle on-period (t_on) of 100 μs and a duty cycle off-period (t_off) of 4 ms in conjunction with a RF generator power output (P_on) of 30 W [39]. Upon plasma extinction, the precursor vapour was allowed to continue to pass through the system for a further 15 min, and then the chamber was evacuated to base pressure followed by venting to atmosphere. Deposed layer thicknesses were approximately 2.3 ± 0.2 μm (deposition rate 160 ± 10 nm min⁻¹).

For conversion to a supported poly(ionic liquid) layer, the pulsed plasma poly(vinylbenzyl chloride) coated substrate was immersed for 120 h at 293 K into a 1 : 6 by volume solution of N-butylimidazole (98 wt.%, Sigma–Aldrich Co.) in dimethylformamide (DMF, 99.5 wt.%, Fisher Scientific UK Ltd.), followed by rinsing in DMF for 16 h. The quaternised surfaces were then immersed for 16 h at 293 K into an aqueous solution comprising 2 M palladium(II) chloride (+99.999 wt.%, Alfa Aesar Co. Ltd.), 3.0 M sodium chloride (+99.5 wt.%, Sigma–Aldrich Co.), and 0.5 M sodium citrate dihydrate (+99 wt.%, Sigma–Aldrich Co.) in high purity water (BS 3978 Grade 1) adjusted to pH 4.5 with citric acid monohydrate (+99 wt.%, Sigma–Aldrich Co.) [40].

2.2. Characterisation

Film thickness values of pulsed plasma poly(vinylbenzyl chloride) deposited onto silicon wafers were measured using a spectrophotometer (model nkd-6000, Aquila Instruments Ltd.). Transmittance–reflectance curves (350–1000 nm wavelength range) were acquired for each sample and fitted to a Cauchy model for dielectric materials [41] using a modified Levenberg–Marquardt algorithm [42]. Reflection-absorption infrared (RAIRS) spectra of pulsed plasma poly(vinylbenzyl chloride) deposited onto silicon wafers were acquired using a FTIR spectrometer (Spectrum One, Perkin–Elmer Inc.) fitted with a liquid nitrogen cooled MCT detector operating at 4 cm⁻¹ resolution across the 400–4000 cm⁻¹ range. The instrument included a variable angle reflection-absorption accessory (Specac Ltd.) set to a grazing angle of 66° for silicon wafer substrates and adjusted for p-polarization. Attenuated total reflectance (ATR) infrared spectra of vinylbenzyl chloride precursor were obtained using a Golden Gate accessory (Specac Ltd.).

Surface elemental compositions of pulsed plasma poly(vinylbenzyl chloride) deposited onto silicon wafers and PTFE membrane were measured by X-ray photoelectron spectroscopy (XPS) using a VG ESCALAB II electron spectrometer equipped with a non-monochromated Mg Kα X-ray source (1253.6 eV) and a concentric hemispherical analyser. Photoemitted electrons were collected at a take-off angle of 20° from the substrate normal, with electron detection in the constant analyser energy mode (CAE, pass energies of 20 and 50 eV for high resolution and survey spectra respectively). Experimentally determined instrument sensitivity factors were C(1s) : O(1s) : N(1s) : Cl (2p) : Pd(3d) : F(1s) equals 1.00 : 0.35 : 0.70 : 0.37 : 0.06 : 0.25 respectively. The core level binding energy envelopes were fitted using Gaussian peak shapes with fixed full-width-half-maxima (fwhm) and linear backgrounds [43,44]. All binding energies were referenced to the C(1s) − C−H hydrocarbon peak at 285.0 eV [45]. Measurements were repeated at least 3 times. Palladium loading on the catalyst membrane, and amount leached during multiple use studies was measured by ICP-OES (Vista MPX CCD Simultaneous axial ICP-OES, Varian Inc.). Calibration of detected palladium signal intensity to actual palladium content in solution was carried out to an accuracy of 0.01 ppm using reference samples at 1, 2, and 5 ppm, prepared from a 1000 ppm stock solution (26 X 1-Pd(a), MBH Analytical Ltd.) diluted in high purity water (resistance of 18.2 MΩ). Analyte solutions were digested in 5 mL of sulphuric and perchloric acids (95 wt.%, Normapur™, and 65 wt.%, Normatom™ respectively, VWR International Ltd.) using a wet digestion method followed by dilution to 25 mL in high purity water. The detection limit of palladium in these catalysis experiment analyte solutions was 0.1 ppm on a mass basis. Palladium membranes were treated in the same manner to remove the palladium containing poly(ionic liquid)–polymer polymer layer from the PTFE membrane substrate.

2.3. Suzuki–Miyaura carbon–carbon coupling reaction

For palladium–poly(ionic liquid) catalyst membrane heated batch reactor studies of catalysis, B10 borosilicate sample flasks were rinsed with ethanol (+99.8 wt.%, Fisher Scientific UK Ltd.), thoroughly scrubbed using detergent and hot water, followed by immersion for 1 h in a solution comprising sodium hydroxide (99.2 wt.%, Fisher Scientific UK Ltd.), propan-2-ol (+99.5 wt.%, Fisher Scientific UK Ltd.), and high purity water (mass ratio 1 : 20 : 5) in order to remove any organic residue. The flasks were then thoroughly scrubbed using detergent and hot water, rinsed in propan-2-ol, and oven dried at 423 K. A final wash step consisted of immersion for 1 h in a 1 wt% nitric acid bath (70 wt.% in water, Fisher Scientific UK Ltd., further diluted in high purity water), followed by thorough rinsing with high purity water and oven drying at 423 K, to ensure that no palladium transfer occurred between solutions. This rigorous cleaning procedure was undertaken before each reaction.
0.50 ± 0.05 mmol of iodobenzene (98 wt%, Sigma–Aldrich Co.), 0.75 ± 0.01 mmol of phenylboronic acid (95 wt%, Sigma–Aldrich Co.), and 0.99 ± 0.01 mmol of potassium carbonate (98 wt%, Sigma–Aldrich Co.) were weighed out into a borosilicate glass vial. 3 mL of a solution comprising ethanol (+99.8 wt%, Fisher Scientific UK Ltd.) and high purity water in a 2 : 1 vol. ratio was added. The flask was agitated to dissolve the potassium carbonate, and then the catalyst membrane was added (47.9 ± 3.4 μmol catalyst membrane, with 0.304 ± 0.022 μmol of palladium(II) or 0.067 wt.% (32.3 ± 2.3 μg) initial palladium loading as measured by ICP-OES analysis). The flask was agitated to a water cooled condenser, and immersed in a water bath at 343 K for 30 min for the reaction to proceed. The reaction solutions were not stirred in order to prevent abrasive damage to the membrane material (it should be noted this means the reported turnover frequencies (TOF, moles of product per mole of palladium per hour) are a lower estimate as diffusion may also limit reaction rates measured). Afterwards, the flask was removed from the water bath and allowed to cool to room temperature, followed by removal of the catalyst membrane and the solution decanted. The flask was then rinsed twice with 1 mL of chloroform (99.8 wt%, Fisher Scientific UK Ltd.) and the washings were added to the decanted solution. Solutions for gas chromatography (GC) analysis were extracted three times with 3 mL of chloroform, spiked with 4 μg mL⁻¹ decane (0.1 g, +99 wt%, Sigma–Aldrich Co.), and made up to 25 mL with dichloromethane. Product solutions (which did not require extraction) were sealed in screw topped borosilicate glass vials fitted with a PTFE/silicone slit septum. Catalyst membranes were dried in air at 293 K for a minimum of 1 h before reuse with a fresh reactant solution each time. As a control experiment, 0.50 ± 0.05 mmol of 4-methoxyiodobenzeno (98 wt%, Sigma–Aldrich Co.) was substituted for iodobenzene to rule out homocoupled product formation.

For Suzuki–Miyaura carbon–carbon coupling reactions under sonicated flow conditions at room temperature, a custom gravity-fed flow cell was used with the membrane sealed using a compression flange. A solution comprising ethanol (+99.9 wt%, Fisher Scientific UK Ltd.) and high purity water in a 2 : 1 vol. ratio was added to the reactor with a fresh reactant solution each time.


cell was used with the membrane sealed using a compression flange. 3 mL of a solution comprising ethanol (+99.8 wt%, Fisher Scientifi
with the precursor molecule confirmed selective vinyl group polymerisation during pulsed plasma deposition [49]. Characteristic para substituted benzene ring absorbances can be found at 1603 cm\(^{-1}\) and 1490 cm\(^{-1}\) [49]. The band at 1263 cm\(^{-1}\) for both the precursor and plasma deposited polymer corresponds to the \(\text{Cl}^-\text{CH}_2^-\text{CH}_2^-\text{Cl}\) wag mode [49]. This halogen-containing group is a prerequisite for quaternisation leading to the formation of a poly(ionic liquid) layer.

XPS analysis of pulsed plasma deposited poly(vinylbenzyl chloride) onto PTFE membrane detected carbon, chlorine, and low levels of oxygen (attributed to a small amount of atmospheric water absorption [50]), Table 1 and Supplementary information Fig. S2. The absence of fluorine signal confirmed complete coverage of the underlying PTFE membrane (no pinholes).

### 3.2. Palladium–poly(ionic liquid) catalyst membrane

Quaternisation of the pulsed plasma deposited poly(vinylbenzyl chloride) films with N-butylimidazole resulted in the appearance of nitrogen XPS signal at the surface, Table 1 and Supplementary information Fig. S3. The N(1s) binding envelope of the quaternised films could be fitted to a main nitrogen environment at 401.9 ± 0.1 eV corresponding to two equivalent nitrogen centres in positively charged imidazolium rings [39,51,52], Fig. 3 and Scheme 1. The slight shoulder towards lower N(1s) binding energy can be attributed to the reaction of N-butylimidazole with trapped free radicals contained within the plasma deposited layer [36,53]. The Cl(2p) peak envelope could be fitted to two different chlorine atom environments with Cl(2p3/2) binding energy values of 197.3 ± 0.1 eV and 200.6 ± 0.2 eV corresponding to chloride anions and non-quaternised unreacted benzyl chloride groups respectively [54], Fig. 4. Based on these two Cl(2p3/2) binding energy environments, the level of surface quaternisation was calculated to be 52 ± 9% (this is most likely to be an underestimate due to the XPS sampling depth (2–5 nm) also probing the sub-surface [55,56]).

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**Table 1**

<table>
<thead>
<tr>
<th>PTFE Membrane</th>
<th>C/%</th>
<th>N/%</th>
<th>O/%</th>
<th>Cl/%</th>
<th>Pd/%</th>
<th>F/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>29.2</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>70.8</td>
</tr>
<tr>
<td>Pulsed Plasma Poly(Vinylbenzyl Chloride) Functionalised</td>
<td>90.4 ± 0.5</td>
<td>0.4 ± 0.8</td>
<td>9.2 ± 0.3</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Pulsed Plasma Poly(Vinylbenzyl Chloride) Functionalised + Quaternised</td>
<td>83.7 ± 0.7</td>
<td>7.9 ± 0.4</td>
<td>4.1 ± 0.3</td>
<td>4.3 ± 0.3</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Pulsed Plasma Poly(Vinylbenzyl Chloride) Functionalised + Quaternised + PdCl(_2)(aq)</td>
<td>78.6 ± 2.2</td>
<td>6.4 ± 0.6</td>
<td>9.8 ± 2.4</td>
<td>4.3 ± 0.6</td>
<td>0.9 ± 0.1</td>
<td>–</td>
</tr>
<tr>
<td>Control Pulsed Plasma Poly(Vinylbenzyl Chloride) Functionalised + PdCl(_2)(aq)</td>
<td>80.7</td>
<td>–</td>
<td>12.9</td>
<td>6.4</td>
<td>0.0</td>
<td>–</td>
</tr>
</tbody>
</table>

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**Fig. 3.** N(1s) XPS spectra: (a) pulsed plasma poly(vinylbenzyl chloride) deposited onto PTFE membrane and quaternised with N-butylimidazole; and (b) following palladium(II) chloride complexation to (a). Signal intensity is counts per second.

**Fig. 4.** Cl(2p) XPS spectra: (a) pulsed plasma poly(vinylbenzyl chloride) deposited onto PTFE membrane; (b) following quaternisation with N-butylimidazole; and (c) following palladium(II) chloride complexation to (b). Due to spin-orbit coupling, Cl(2p\(_{3/2}\)) components are shifted by 1.6 eV to higher binding energy relative to the Cl(2p\(_{1/2}\)) components, with a Cl(2p\(_{3/2}\)):Cl(2p\(_{1/2}\)) peak area ratio equal to 2:1 [54]. Signal intensity is counts per second.
phenylboronic acid, no other compounds exceeded 1% of the GC biphenyl product peak area), with a catalyst turnover frequency of 3097 ± 323 h⁻¹ (TOF, moles of product per mole of palladium per hour). Over 4 cycles, palladium leaching into the reaction solution was measured to be 83 ± 33 ppb h⁻¹ cm⁻³ (for the initial membrane equivalent reaction solution loading of 11.1 ± 8 ppm on a mass basis (or 0.061 ± 0.004 mol%) — this is equivalent to ~1% of the Pd present leaching from an already sub 0.1 mol% catalyst loading during one reaction cycle at 343 K). This is consistent with the negligible drop in product yield with reaction cycle number, Supplementary information Fig. S4.

As a control, the Suzuki–Miyaura coupling reaction was run using 4-methoxyiodobenzene and phenylboronic acid reactants under similar reaction conditions in order to rule out the possibility of homocoupled by-product formation. GC–MS analysis of the obtained products showed the presence of only 4-methoxybiphenyl, and an absence of homocoupled biphenyl by-product.

3.3.2. Room temperature sonicated membrane flow catalysis

The practical viability of these palladium–poly(ionic liquid) catalyst membranes for continuous flow Suzuki–Miyaura carbon–carbon coupling reactions was demonstrated by allowing the reaction solution to permeate into the membrane during sonication at room temperature (sonication speeded up the liquid flow rate). After 1 h of reaction time, 17 mol% (0.17 mmol of 1.0 mmol) of the iodobenzene reactant present in the starting solution had been transported through the catalytic membrane as either product or unreacted iodobenzene. The collected solution contained only aromatic organic compounds (54 mol% biphenyl product, 42 mol% iodobenzene, and 4 mol% phenylboronic acid — no other components exceeded 3% of the GC biphenyl product peak area). This indicates that iodobenzene (either unreacted or as carbon–carbon coupled biphenyl product) preferentially passes through the membrane relative to phenylboronic acid. The TOF (calculated as before) for biphenyl product formation was found to be 154 h⁻¹.

For this system also, a control Suzuki–Miyaura coupling reaction run using 4-methoxyiodobenzene and phenylboronic acid reactants under similar experimental conditions showed an absence of homocoupled biphenyl by-product (only 4-methoxybiphenyl detected), thereby ruling out the possibility of homocoupled by-product formation.

4. Discussion

Pulsed plasmachemical functionalisation of solid surfaces using polymerisable functional precursors is a well-established, solventless, single-step, conformal, and substrate-independent technique, which offers the advantage of high levels of functional group retention [59], thus making it well-suited for the preparation of membrane supported poly(ionic liquid) catalysts. Infrared spectroscopy and XPS analyses have shown that there is a high level of chloro- group and benzene ring retention during pulsed plasma deposition of vinylbenzyl chloride precursor, thereby facilitating the subsequent step of quaternisation with N-butylimidazole to form a poly(ionic liquid) layer, Scheme 1, Figs. 2–4. Complexation of this surface to palladium chloride yields a palladium containing poly(ionic liquid) catalyst membrane.

Although high TOFs are achievable with conventional dispersed homogeneous and heterogeneous palladium catalyst systems [60–63], such materials suffer from the drawback of requiring post reaction recovery of the palladium catalyst or higher palladium loadings. The practical viability of the palladium–poly(ionic liquid) catalyst membranes in the present study has been demonstrated for the Suzuki–Miyaura coupling reaction of iodobenzene. The measured TOF value of 3097 ± 323 h⁻¹ for heated (343 K) batch reaction mode is comparable with previously reported homogeneous ionic liquid catalysts (TOFs of 10⁵–10⁶ h⁻¹) [4,5,7,9,10] and other heterogeneous poly(ionic liquid) catalysts (TOFs of 10⁻¹–10⁻³ h⁻¹) [12–15].

The palladium membrane loadings used for the Suzuki–Miyaura coupling reaction (a reaction solution equivalent of 0.061 ± 0.004 mol % or 11.1 ± 8 ppm on a mass basis) are lower than most previously reported ionic liquid catalysts (homogeneous and heterogeneous) which range between 0.1–18 mol% [5,7–12,14–16,22,64]. A palladium leaching value of 83 ppb h⁻¹ cm⁻³ at 343 K compares favourably with previously reported solid support heterogeneous catalysts (where palladium leaching rates exceed 100 ppb h⁻¹ cm⁻³) [65,66]. This is equivalent to ~1% of the Pd present leaching from an already sub 0.1 mol% catalyst during one reaction cycle at 343 K, and even lower leaching rates are to be expected when the membrane is used at room temperature.

In the case of the flow membrane reactor mode of operation, ambient temperature sonicated Suzuki–Miyaura reactions gave a calculated TOF value for biphenyl product formation of 154 h⁻¹. This is comparable with previously reported Suzuki–Miyaura flow reactors (TOF 10¹ to 10⁴ h⁻¹) [24,26–28,67], however such systems require high pressures or elevated temperatures. The beneficial preferential separation of iodobenzene reactant and biphenyl product from the phenylboronic acid and reaction solvents in the present study can be ascribed to the selective solubility of the prepared membrane system, Scheme 3. Ionic liquids tend to solvate a wide range of species including unsubstituted benzene and haloarenes [68,69], therefore iodobenzene can diffuse directly through the poly(ionic liquid) layer, accounting for its high concentration in the product solution. Comparatively, phenylboronic acid is insoluble in some imidazolium ionic liquids and will therefore predominantly remain behind in the reactant ethanol:water solvent phase [70]. The absence of transportation for the water and ethanol reaction mixture constituents through the catalyst membrane is most probably due to the immiscibility of ethanol and water with imidazole containing ionic liquids and the pulsed plasma deposited poly(vinylbenzyl chloride) interfacial layer at ambient temperature [71–73], as well as liquid repellency from the underlying PTFE membrane (surface tension of water = 72.8 mN m⁻¹ [74], surface tension of ethanol = 22.3 mN m⁻¹ [74], and surface energy of PTFE = 20.0 mN m⁻¹ [75]). Therefore, the outlined approach not only allows for the palladium catalysed Suzuki–Miyaura carbon–carbon coupling reaction to proceed at room temperature under flow conditions, but also concurrently separates the solvent mixture from the aromatic product phase, thereby eliminating any need for post reaction separation of product from reaction solvents.

5. Conclusion

Plasmachemical surface functionalisation with benzyl chloride groups provides a quick, low cost approach for fabricating anisotropic palladium–poly(ionic liquid) catalyst membrane systems. This


