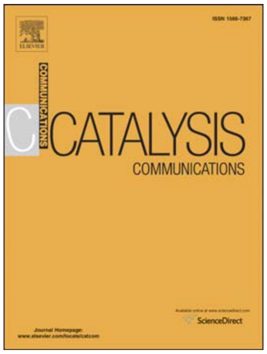

Highly organic phase soluble polyisobutylene-bound cobalt phthalocyanines as recyclable catalysts for nitroarene reduction

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Highly Organic Phase Soluble Polyisobutylene-Bound Cobalt Phthalocyanines as Recyclable Catalysts for Nitroarene Reduction

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Abstract

A cobalt phthalocyanine (CoMPc) containing covalently linked polyisobutylene (PIB) groups as phase anchors that is both highly soluble in nonpolar organic solvents and phase selectively soluble in a liquid/liquid separation step is shown to be an effective recyclable homogeneous catalyst for nitroarene reduction in a semi-thermomorphic system. Electron-donating and electron-withdrawing substituents in the nitroarene are tolerated in this aniline synthesis and the catalyst is recyclable up to 10 cycles with little leaching and no detectable loss in reactivity after 10 cycles.

Keywords

Thermomorphic; Metallophthalocyanine catalyst; Polyisobutylene; Nitroarene reduction; Catalyst recycling

1. Introduction

Aromatic amines are important organic compounds due to their use in the syntheses of dyes [1], pesticides [2], pharmaceuticals [3,4], and polymers [5]. Reduction of nitro compounds is one of most widely used routes to this class of compounds. Classically reduction of nitroarenes to form anilines uses hydrogenation with Pd/C [6]. More recently, there has been an increase in interest in homogeneous catalysts that use more earth abundant metals [7-9], that are recyclable [10,11], or that use alternatives to hydrogen as the penultimate reductant [12-15].

Metallophthalocyanines (MPcs) were originally developed as pigments [16] but are now also used as photosensitizers, photodynamic therapy agents, and in molecular electronics [17,18]. MPcs can also be used as catalysts. However, their use in homogeneous catalysis is less common than is the case for porphyrins [19-21]. MPcs are less commonly used as homogeneous catalysts because MPcs have solubility that is in the range of 10^{-5} to 10^{-7} M in organic solvents [22], a limitation that renders their use as homogeneous catalysts problematic. Our success in synthesis of PIB-bound MPcs that dissolve in hydrocarbon polymers and the activity of several MPcs as heterogeneous catalysts for nitroarene reduction [23,24] suggested to us that PIB-modified MPcs could be recyclable homogeneous catalysts and that this hypothesis could be tested by examining their use in nitroarene hydrogenation. Our hypothesis about the solubility and activity of PIB-modified MPcs has proven correct and we have shown here that a PIB-bound CoMPc catalyst can be used as a homogeneous catalyst for nitroarene reduction and that this catalyst can be quantitatively separated from products and recycled as discussed below.

2. Experimental

2.1. General procedures

Vinyl terminated PIB (Glissopal 1000) was provided by BASF [25]. Other reagents and solvents were purchased from commercial sources and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on Inova 300 or 500 MHz NMR spectrometers. IR spectra were obtained using a Shimadzu Affinity-1S IR spectrometer. UV–Visible spectra were recorded on a Shimadzu UV-2600 spectrophotometer. A NexION 300D Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) was used to determine the Co metal content in **6**.

2.2. Synthesis of **2-6**

The syntheses of **2-6** are detailed in the supplemental information along with ^{1}H and ^{13}C NMR spectroscopic data.

2.3. General procedure for nitroarene reduction using hydrazine hydrate with **6** as a homogeneous catalyst

A biphasic mixture of 1 mmol of nitroarene and 0.4 mol% of catalyst **6** was prepared using 5 mL of heptane and 5 mL of anhydrous ethylene glycol in a Schlenk tube. Then 5 equivalent of hydrazine hydrate were added and the biphasic solution was stirred at 110 ^{o}C under a N_2 atmosphere for 24 h. While the original biphasic mixture never became a single phase during this process, the ethylene glycol phase visually appeared to increase in volume due to some heptane dissolution. In addition, some of the PIB-bound MPc complex visually was present in that phase. After the reaction was complete, the biphasic mixture was cooled down to ambient temperature. The polar ethylene glycol-rich phase was separated from the heptane solution of the MPc and the product was isolated by chromatography from this polar phase. The catalyst in the heptane phase was recycled for further experiments after addition of fresh reagents and fresh ethylene glycol.

4-Chloroaniline. ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.10 (2 H, d, *J* = 8.8 Hz), 6.60 (2 H, d, *J* = 8.8 Hz), 3.50-3.80 (2 H, br); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.90, 129.08, 123.12, 116.20.

4-Bromoaniline. ^{1}H NMR (300 MHz, $CDCl_3$), δ 7.23 (2 H, d, *J* = 8.4 Hz), 6.56 (2 H, d, *J* = 8.4 Hz), 3.60-3.70 (2 H, br); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.37, 131.97, 116.67, 110.15.

4-Aminobenzoic acid. ^{1}H NMR (500 MHz, DMSO- d_6), δ 7.59 (2 H, d, J = 8.5 Hz), 6.54 (2 H, d, J = 8.5 Hz), 5.70-5.84 (2 H, br); ^{13}C NMR (125 MHz, DMSO- d_6) δ 168.42, 153.64, 131.88, 117.41, 113.34.

4-Aminotoluene. ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.02 (2 H, d, J = 8.5 Hz), 6.65 (2 H, d, J = 8.5 Hz), 3.50-3.60 (2 H, br), 2.30 (3 H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.74, 129.63, 127.59, 115.13, 20.34.

4-*tert*-Butylaniline. ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.19 (2 H, d, J = 9.0 Hz), 6.65 (2 H, d, J = 9.0 Hz), 3.50-3.60 (2 H, br), 1.28 (9 H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.70, 141.32, 125.97, 114.87, 33.83, 31.46.

4-Aminophenol. ^{1}H NMR (500 MHz, DMSO- d_6), δ 8.50-8.55 (1 H, br), 6.46 (2 H, d, J = 9.0 Hz), 6.42 (2 H, d, J = 9.0 Hz); ^{13}C NMR (125 MHz, DMSO- d_6) δ 148.79, 140.89, 116.19, 116.111.

1,4-Diaminobenzene. ^{1}H NMR (500 MHz, DMSO- d_6), δ 6.57 (4 H, s), 3.25-3.40 (4 H, br); ^{13}C NMR (125 MHz, DMSO-d_6) δ 138.56, 116.70.

1-Aminonaphthalene. ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.82-7.89 (2 H, m), 7.48-7.55 (2 H, m), 7.34-7.41 (2 H, m), 6.79-6.82 (1 H, m), 4.10-4.20 (2 H, br); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.00, 134.28, 128.44, 126.26, 125.75, 124.74, 123.53, 120.72, 118.83, 109.57.

3. Results and discussions

In our initial studies, we first repeated others' work that used an insoluble CoMPc as a heterogeneous catalyst in ethylene glycol to reduce 4-chloronitrobenzene using hydrazine hydrate as the reducing agent [26]. However, extension of this work using the PIB-supported CoMPc **1** (Fig. 1) [27] in this same solvent or in mixtures of polar solvents and heptane failed or led to incomplete reduction of 4-chloronitroarene after 24 h at 80 °C (cf. Table S1). We addressed this problem by preparing a CoMPc with PIB groups connected to the phthalocyanine core by electron-withdrawing groups (Scheme 1). Starting with a thiol-ene reaction of vinyl-terminated PIB [28,29] with thioacetic acid, PIB thioacetate **2** was prepared. Hydrolysis of **2** formed the thiol PIB-SH **3** [30] that was allowed to react with 4-nitrophthalonitrile in a nucleophilic aromatic substitution reaction to form the PIB-thiophthalonitrile **4** [31]. Oxidation of **4** with *m*-chloroperbenzoic acid formed the PIB_{1240} sulfonyl phthalonitrile **5** [32]. Tetracyclization of **5** in the presence of $CoCl_2$ then formed the desired PIB_{1240}-bound MPc **6** [33]. The phthalocyanine **6** so formed is a mixture of species with PIB in different orientations in the four quadrants of the phthalocyanines. As a result, analysis affords a nondescript ^{1}H NMR spectrum. However, **6** was characterized by inductively coupled mass spectroscopy (ICP-MS) and UV-Visible spectroscopy. ICP-MS analysis of a 1 g sample of **6** showed that it contained 0.0087 g of cobalt. This corresponds to an M_n of 6770 Da that is higher than expected based on a ^{1}H NMR spectroscopic analysis of the M_n of **5**. This analysis of **5** compared the integrated intensity of a known amount of 1,1,2,2-tetrachloroethane internal standard to the integration for the signals for the three aryl protons of **5** at 8.34, 8.29, and 8.07 δ and the two protons in the $–CH_2SO_2$ doublet of doublets of **5** at 3.13 and 2.99 δ of the PIB group and showed that **5** had a d.p. of 22 (a M_n of 1430 Da). This degree of polymerization is higher than that of the starting thioacetate **2** which by a ^{1}H NMR analysis had PIB groups with a d.p. of 20. The difference between **2** and **5** reflects fractionation of the PIB-bound species during the synthesis and purification steps in Scheme 1. The purification steps leading to isolation of **6** either formed **6** with PIB groups with d.p.s of 26 or formed some **6b** that did not contain Co. If we conservatively assume no further fractionation occurred in forming **6** from **5**, we calculate that **6** is ca. 87% metalated. Complex **6** has a λ_{max} at 669 nm that is slightly higher than that reported previously for **1** (λ_{max} = 675 nm) (Fig. S1). This peak corresponds to the Q band of the MPc. The shift of the Q band of **6** at 675 to the 669 nm band of **1** is consistent with the introduction of an electron-withdrawing sulfonyl substituent.

Gratifyingly, the conversion of 4-chloronitrobenzene to 4-chloroaniline was 100% based on ^{1}H NMR spectroscopy when complex **6** was used as catalyst in the presence of 5 equivalents of hydrazine hydrate instead of **1** (Scheme 2). In these experiments, the reduction was carried out over a period of 24 h at 110 °C using a 1/1 (vol/vol) mixture of a 4.0×10^{-4} M heptane solution of **6** and ethylene glycol. Under these reactions conditions, the solution never becomes monophasic but it is rather partially thermomorphic – the volume of the denser phase visually increases and some of **6** dissolves in this phase based on a slight color change of the ethylene glycol rich phase. Fully thermomorphic systems including a 3/1 heptane/ethanol mixture, heptane/glyme (1/1, vol/vol) and heptane/*n*-propanol (1/1, vol/vol) were also examined but reductions in these solvent mixtures only led to 83-95% conversion of the nitroarene to aniline. Other thermomorphic systems using *N*,*N*-dimethylformamide, benzyl alcohol, and glycerol with heptane were even less successful. Control experiments without any catalyst or with a PIB-bound metal free phthalocyanine formed no product aniline. Thus, in subsequent studies of the generality and recyclability of **6** in reductions of nitroarenes at 110 ^{o}C, **6** was selected as the catalyst, 5 equivalents of hydrazine hydrate was used as the reducing agent, and 1/1 (vol/vol) mixture of heptane and ethylene glycol was used as the solvent mixture.

Table 1 Reduction of nitroarenes to corresponding aminoarenes and recyclability of **6** in ten cycles of nitroarene reduction (Scheme 2)[a, b]

Entry	Nitroarene	Yield in each cycle[c]					
		1	2	3	4	5	6-10[d]
1	4-chloronitrobenzene	74	74	74	73	72	75
2	4-bromonitrobenzene	63	71	73	76	75	71
3	4-nitrotoluene	56	81	79	82	78	80
4	4-*tert*-butylphenylnitrobenzene	68	84	77	81	82	86
5	4-nitrobenzoic acid	70	72	70	75	74	79
6	4-nitrophenol	50	69	69	68	68	65
7	4-nitroaniline	46	69	72	71	65	74
8	1-nitronaphthalene	75	-	-	-	-	-

[a] 1 mmol of nitroarene, 4×10^{-3} mmol of **6**, and 5 mmol of hydrazine hydrate were dissolved in 5 mL of ethylene glycol and 5 mL of *n*-heptane and this mixture was stirred at 110 °C under a nitrogen atmosphere for 24 h. [b] After the nitroarene had been completely reduced (as determined by ^{1}H NMR spectroscopy), the reaction mixture was cooled and the bottom product-containing layer was removed. Fresh nitroarene, hydrazine hydrate, and ethylene glycol were added to the flask for a subsequent cycle. [c] The yields reported are isolated yields of products that were pure by ^{1}H and ^{13}C NMR spectroscopy. The product anilines were obtained by extracting the arylamine product from the ethylene glycol phase using ethyl acetate and further purified using column chromatography. [d] The yields for cycles 6-10 are an average yield for each of these five cycles based on the total isolated yield for a combination of the product from the ethylene glycol phases for cycles 6-10.

The generality of this reduction and recyclability of these catalysts was tested with varied aryl substituents on nitroarenes as shown in Table 1. 4-Chloro- and 4-bromonitrobenzene gave high isolated yields and complete conversion of the starting nitroarene. Yields of 4-methyl- and 4-*tert*-butylaniline were slightly lower in cycle 1, possibly due to the solubility of these aniline products in the heptane phase. Nitroarenes with electron donating substituents like hydroxy and amino substituents also were quantitatively converted to aniline products affording comparable isolated yields. Reduction of 1-nitronaphthalene was also successful. However, this reduction product is a known carcinogen so repetitive cycles were not performed. Consistent yields cycle-to-cycle were however observed for all the nitroarenes studied, reflecting the high thermal and chemical stability associated with MPcs like **6** and the high phase selective solubility of **6**. This stability as well as the phase selectivity of **6** due to the PIB support also makes it simple to recycle and to separate the homogeneous catalyst **6** from the aniline products.

Recycling of the cobalt catalyst **6** was accomplished by cooling the reaction mixture to ambient temperature. The less dense heptane-rich phase containing **6** was then physically separated by a gravity separation from the ethylene glycol phase containing the product. The product was isolated from this ethylene glycol phase. Visually no leaching of **6** into the ethylene glycol was seen in any of the 10 recycling experiments with any of the 7-nitroarene substrates in Table 1 with the product phase being a light yellow color. This qualitative observation of the absence of leaching was confirmed by UV spectroscopic analysis of the product phase for the first cycle for the 4-chloronitrobenzene reduction. While the product phase in these reactions has a yellow color, we were able to use UV-visible spectroscopy to quantitatively asses leaching since **6** has a strong absorbance at 640 nm. These experiments showed that the leaching of **6** into the product phase after the first cycle was <0.05 % of the charged catalyst **6**. An additional UV experiment was carried using the catalyst isolated from the tenth cycle of a 4-chloronitrobenzene reduction which showed that the recovered catalyst had <0.01% leaching into ethylene glycol.

The catalyst-containing heptane phase was reused by simply adding a new batch of nitroarene and hydrazine hydrate in ethylene glycol to the recovered heptane solution of **6**. As shown in Table 1, **6** was able to catalyze at least 10 cycles of reaction with each substrate without significant changes in isolated yield of product.

To confirm that the catalyst **6** had unchanged activity through these ten cycles, we carried out kinetic studies following the conversion versus time for reductions of 4-chloronitrobenzene and 4-nitrobenzoic acid as substrates in a cycle 11 and compared this plot to a similar conversion versus time plot for cycle 1 (Fig. 2). In these experiments, we first carried out a reaction using a known amount of **6** in heptane and ethylene glycol and a substrate nitroarene, following the conversion of the nitroarene versus time by ^{1}H NMR spectroscopy. Then, after the tenth cycle, we isolated the PIB-bound catalyst **6** from the heptane-rich solution. The same amount of this catalyst **6** as was used in the reaction with fresh catalyst was then used in an eleventh cycle and the conversion versus time was compared to the plot obtained with fresh catalyst. As shown in Fig. 2, the conversion versus time between the first and the eleventh cycle are unchanged for both substrates, indicating that the catalyst activity had not changed during these ten cycles and separations. This is consistent with lack of change in isolated yields of products in Table 1 and with the expected stability of the MPc catalysts.

Finally, we examined the spectrum of **6** by UV-Visible spectroscopy looking both at fresh **6** and at **6** that was isolated after eleven cycles of reduction and separation. As shown in Fig. 3, there is no obvious change in the visible spectrum of **6** after eleven cycles of 4-chloronitrobenzene reduction and separation.

4. Conclusions

In summary, a highly heptane and organic solvent soluble PIB-supported CoMPc was synthesized and was shown to be an effective and recyclable homogeneous catalyst for reduction of nitroarenes using hydrazine hydrate as a reducing reagent under semi-thermomorphic conditions at 110 ˚C. While a variety of solvents yielded product, the use of an equivolume mixture of ethylene glycol and heptane as solvents worked best. The isolated yields of the reduced aniline products were consistently good for ten cycles with a variety of electron-donating and electron-withdrawing substituents on the starting nitroarene. Because of the PIB-induced phase selective solubility of the PIB-supported CoMPc, the catalyst can be recycled at least 10 times. Kinetic studies show the catalyst has unchanged reactivity and UV-visible spectroscopy shows no change in catalyst structure, results consistent with the expected thermal and kinetic stability of MPc catalysts. We believe the solubility induced into these MPcs by PIB groups can be employed to make other PIB-bound MPcs similarly useful in other homogeneously catalyzed processes where a similar biphasic catalyst/product solution separation can facilitate both catalyst/product separation and recycling.

Acknowledgements

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Fig. 1. A PIB-bound CoMPc complex that is soluble at 10 wt% in heptane or CH_2Cl_2 at 25 ^{o}C.

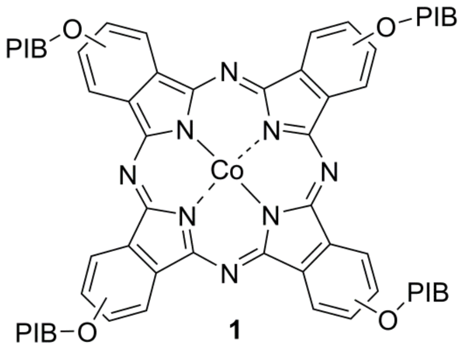

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Fig. 2. Conversion versus reaction time profile for the first and eleventh cycle for nitroarene reductions catalyzed by **6** with two different nitroarenes: (a) 4-chloronitrobenzene and (b) 4-nitrobenzoic acid.

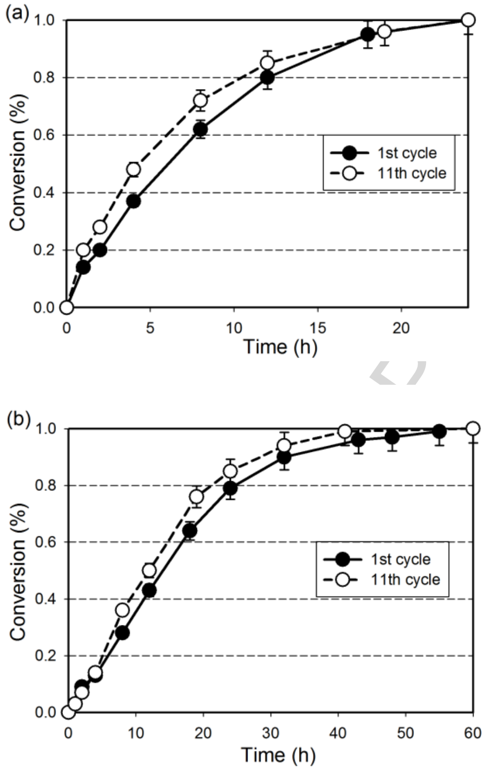
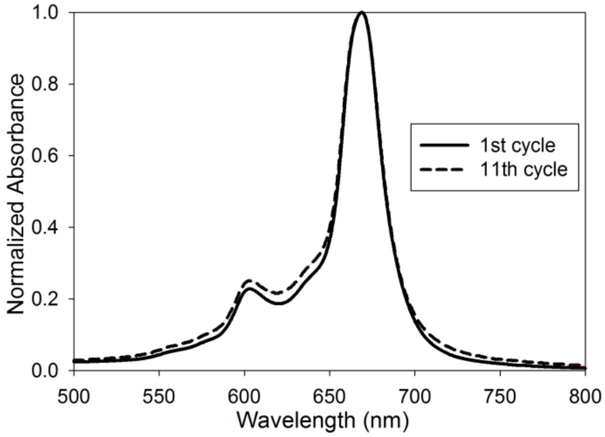
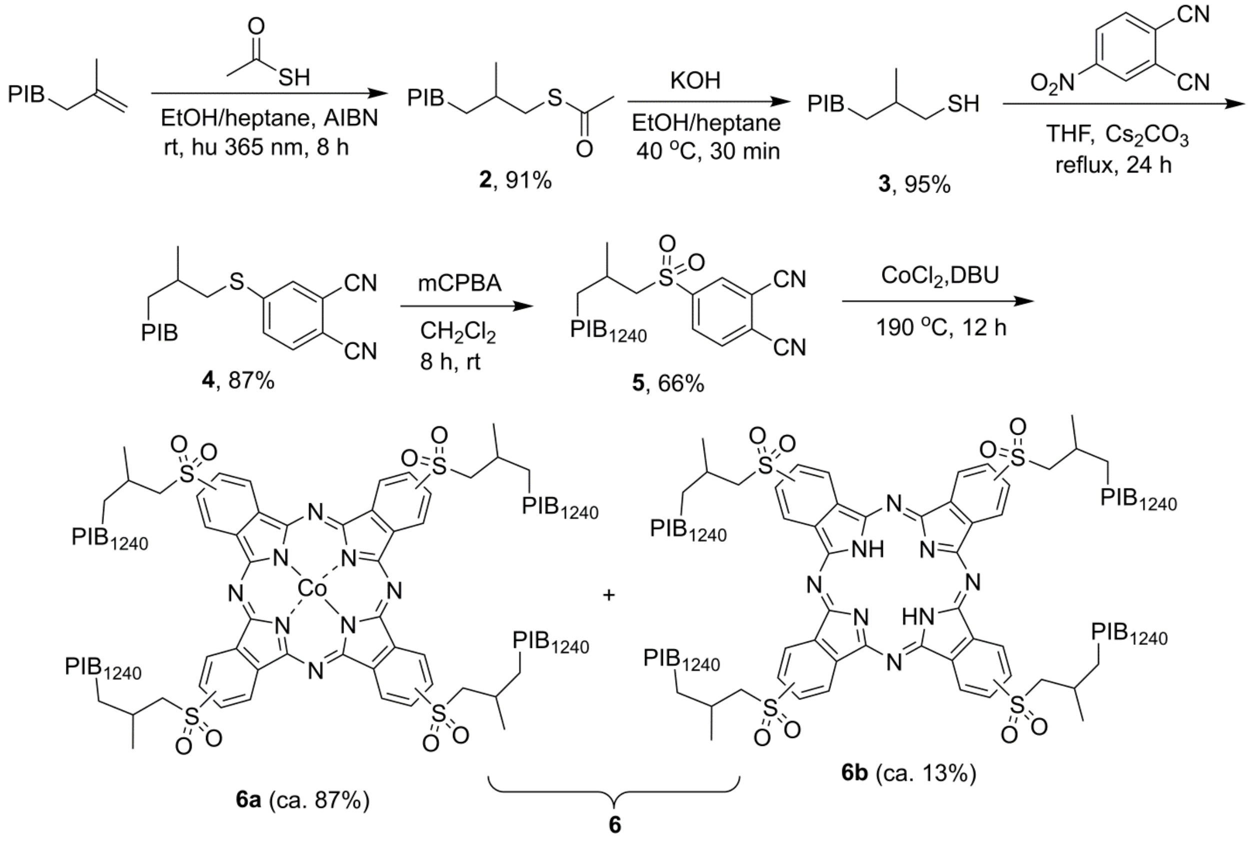
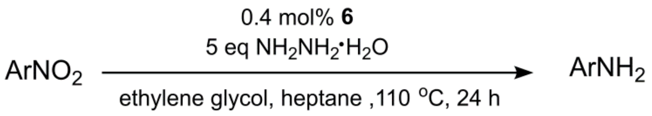


Fig. 3. UV-Vis spectrum of a heptane solution of **6** before and after eleven cycles of 4-chloronitrobenzene reduction.



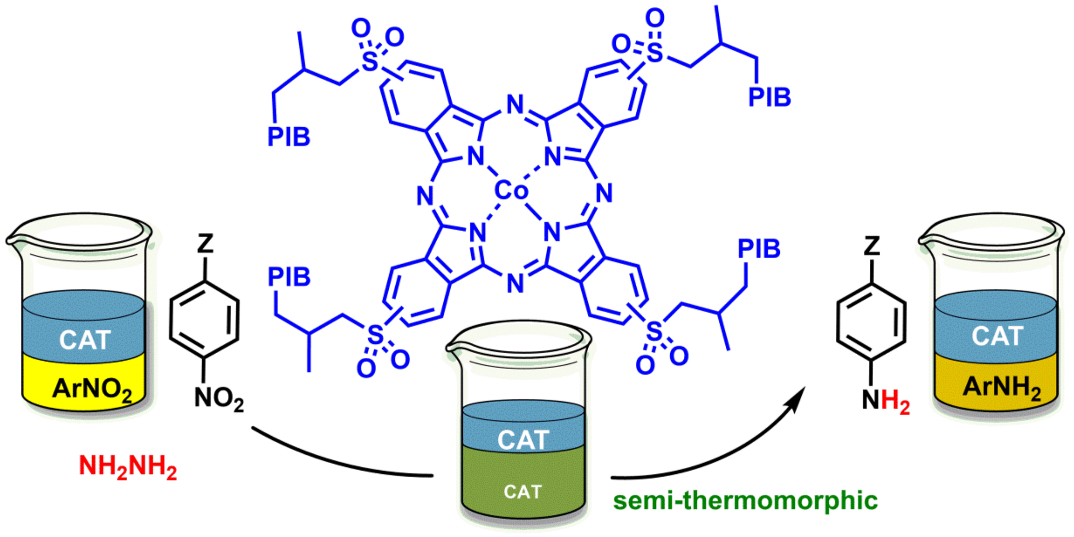
Scheme 1. Synthesis of **6**.





$$\mathrm{ArNO_2} \xrightarrow[\text{ethylene glycol, heptane ,110 °C, 24 h}]{\text{0.4 mol\% } \mathbf{6} \\ \text{5 eq } \mathrm{NH_2NH_2{\cdot}H_2O}} \mathrm{ArNH_2}$$

Scheme 2. Nitroarene reduction using the heptane-soluble PIB-bound cobalt phthalocyanine catalyst **6**.



Graphical Abstract

Highlights

- A new highly soluble polyisobutylene supported cobalt phthalocyanine complex was synthesized.
- This CoMPc was shown to be a homogeneous catalyst for nitroarene reduction.
- This CoMPc catalyst could be separated from products by liquid/liquid separation.
- This CoMPc catalyst was recyclable with very low leaching and no loss in reactivity