Catalytic oxidation of anilines into azoxybenzenes on mesoporous silicas containing cobalt oxide

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ABSTRACT

Synthesis of cobalt-bound copolymers and the use of this polymer as a template to prepare mesoporous silicas containing cobalt oxide are reported. This material catalyzed the oxidation of anilines into the corresponding azoxybenzene efficiently with the hydrogen peroxide as the oxidant. Furthermore, the catalyst can be recycled without losing the activity.

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1. Introduction

Azoxybenzene and its derivatives represent a new class of compounds displaying a broad range of potential application in materials because they have characteristic features emerging from the conjugated systems and polar functionality [1]. In addition, this type of compounds is the precursor for Wallach rearrangement, which offers a simple way to prepare hydroxyazobenzenes [1a,2]. Generally, the preparation of azoxybenzenes is via the direct oxidation of the corresponding azobenzene (Eq. (1)) and many oxidizing agents such as hydrogen peroxide [3], dimethyldioxirane [4], sodium perborate [5] and peracid [6] have been used for this process. In the use of H_2O_2, Murray and coworkers found that the metal complex ($MeReO_3$) accelerated the oxidation to provide excellent yields of azoxybenzenes [3].
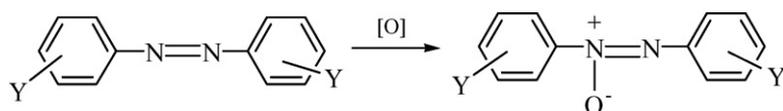
Azoxybenzene is known to be the intermediate from the oxidation of aniline or the reduction of nitroarene via the condensation of nitrosobenzene with N-phenylhydroxyamine. The oxidation steps of aniline leading to nitrobenzene are quite complex and a generally accepted mechanistic pathway is depicted in Scheme 1 [7]. Thus, manipulation of reaction conditions leading to the azoxy compound as a single product becomes a research interest for chemists. Till now, a few catalytic systems developed for this purpose have been reported [8–10]. Typically, these are perfluoroketone-silicate [8], polyoxometalate of a sandwich type structure [9] and titanium silicalite-1 (TS-1) [10]. Continuing our research on catalysis, we have developed a preparation of cobalt-containing mesoporous silica, which is active for the conversion of anilines into azoxybenzenes.

$$(1)$$

2. Results and discussion

2.1. Preparation of catalyst

The cobalt-containing silicas (denoted as Si-Co) were synthesized through the condensation of tetraethoxysilane templated

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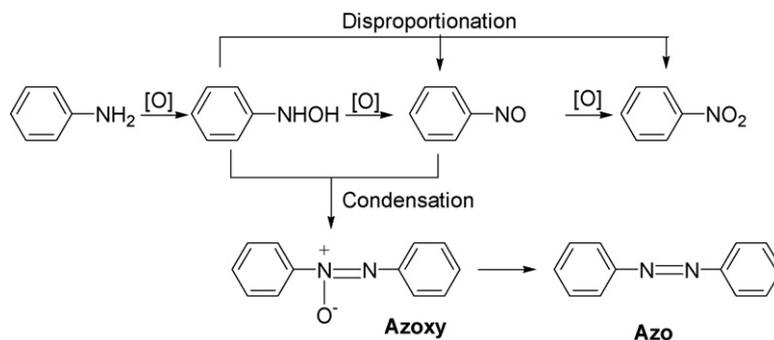
Scheme 1. Mechanistic pathway for oxidation of aniline.
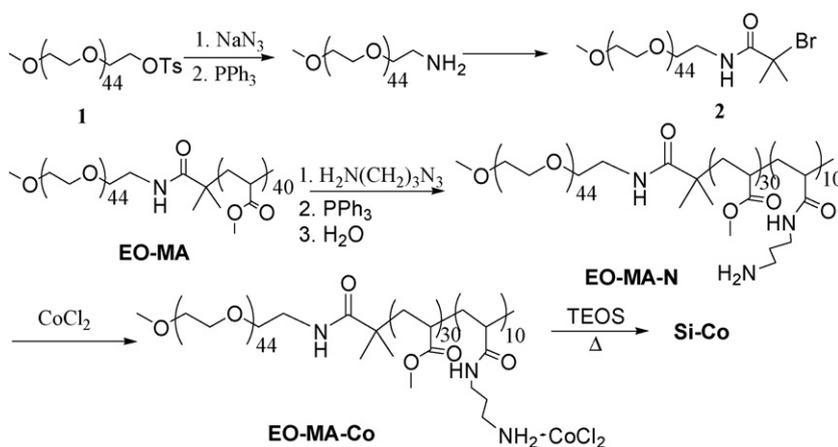
Scheme 2. Preparation of the metal-containing diblock copolymer.

by the amphiphilic diblock (EO-MA-Co) copolymer under acidic conditions [11]. Starting with the tosylate of the methyl-capped polyethylene oxide $Me(OCH_2CH_2)_{45}OTs$ (**1**), the tosylate function was transformed into an amine function, which subsequently reacted with 2-bromoisobutyric chloride to provide the macro-initiator poly(ethylene oxide)-2-bromoisobutyrate (**2**) (Scheme 2). The formation of the amide linkage is required for keeping the copolymer intact during the further transformation of the diblock copolymers. A simple ester linkage formed from $Me(OCH_2CH_2)_{45}OH$ and 2-bromoisobutyric chloride would undergo hydrolysis during the reactions. Compound **2** was subjected to connection with the poly(methyl acrylate) chain by the atom transfer radical polymerization method [12]. In a typical run, the reaction of macro-initiator (3.3 mmol) and methyl acrylate (MA) (55 mmol) at 30 °C for 10 min resulted in the formation of the desired EO-MA of $M_N = 4500$ (PDI = 1.14). Based on the GPC and ^{1}H NMR integration, the polymerization degree of MA is in an average of 40 units. Treatment of the diblock copolymer with 3-aminopropyl azide provided the copolymer with the amido-linked side chain. The composition of the resulting modified copolymer (EO-MA-N), determined by ^{1}H NMR integration, included a 0.25-mole fraction of the azido group. Under anhydrous conditions, the copolymer reacted with triphenylphosphine to generate the iminophosphorane functionality [11,13], which was subsequently hydrolyzed to generate the amine function. Addition of $CoCl_2$ to an aqueous solution of the copolymer readily caused the color change from purple into blue, indicating the formation of its metal complex (EO-MA-Co).

By using the metal-bound diblock copolymer EO-MA-Co as the template, preparation of the desired materials under acidic conditions was achieved. Upon calcination at 560 °C, the porous

silica Si-Co was obtained. X-ray diffraction patterns of the sample show that the mesophase of the resulting porous silica is disordered. However, nitrogen absorption–desorption isotherms (Fig. 1) showed that the pore dimension of Si-Co is 13.3 nm with surface area of 499 m^2/g, typical of mesoporous materials and similar to those of related materials [11]. The content of cobalt species inside of channels was estimated to be 16.5 mg/g of silica via the analysis of ICP-mass determination. XPS analysis was carried out in order to determine the valence state of the cobalt species on silicas. The O 1s XPS peak at 531.8 eV was attributed mainly to the silicates. A detailed scan of the Co $2p_{3/2}$ area showed a peak at 783.3 eV, which is assigned to the binding-energy component of the cobalt oxide
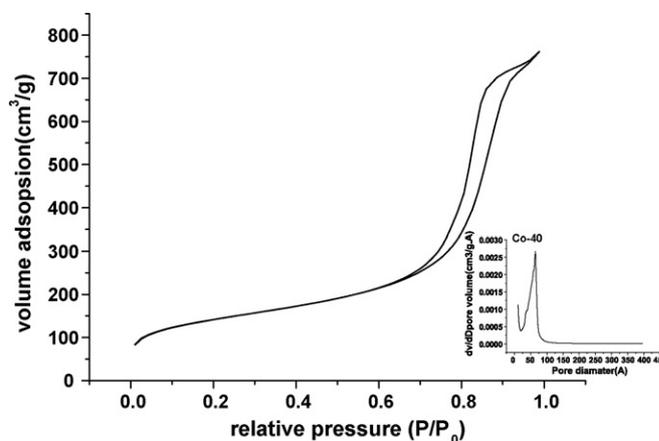
Fig. 1. Nitrogen absorption–desorption of Si-Co.

Fig. 2. SEM image of Si-Co.

Fig. 3. Reaction profile for the oxidation of aniline at 80 °C in the presence of Si-Co: (○) azoxybenzene and (■) aniline.
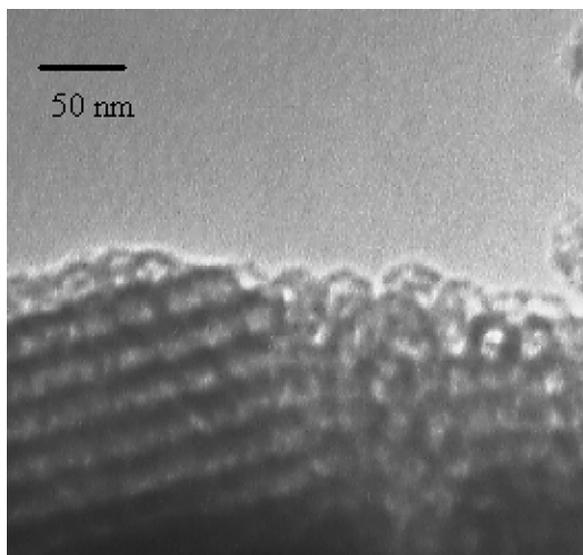
(CoO). This value is consistent with the related species on metal oxide surface [14].

Fig. 2 shows the scanning electron microscopy (SEM) images of the prepared silicas. It was observed clearly that spherical morphology predominated in Si-Co. They were uniform in size and the average size of the spheres was around 20 nm. Furthermore, no agglomeration of cobalt oxide could be observed on the surface of mesoporous silicas, suggesting a well-dispersed manner of the metal complex.

2.2. Catalysis

Oxidation of anilines with hydrogen peroxide over Si-Co was investigated. The oxidation of aniline served as a model reaction (Eq. (2)) for studying the influence of catalysts and critical reaction parameters such as solvent, oxidant and temperature. Results are summarized in Table 1.

$$\text{(2)}$$
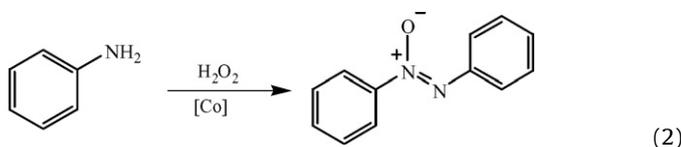
When hydrogen peroxide (10 mmol) was added to a solution of aniline (5 mmol) and Si-Co in acetonitrile (1 mL) under air atmosphere at 25 °C, azoxybenzene was obtained in 26% by GC analysis (entry 1). While optimizing the reaction conditions, we found that the yield of the desired product increased by increasing the amount of H_2O_2 (entries 2 and 3). However, the use of excess of reagents does not meet the economy of chemical reactions. This can be solved by raising the reaction temperature. Thus the yield reached to 78% at 55 °C, and 98% at 80 °C. Running the reaction without Si-Co or with the use of a simple porous silica (SBA-15) with $CoCl_2$ gave no desired product or poor yields (entries 6–8), indicating the necessity of the porous catalyst Si-Co.

As for the solvent effect, both water and acetonitrile are good choices. Providing the excellent yield in aqueous solution of this oxidation does meet the context of green chemistry. However, running in an aqueous medium gave also a trace amount of azobenzene as the side product at a higher reaction temperature (entry 15).
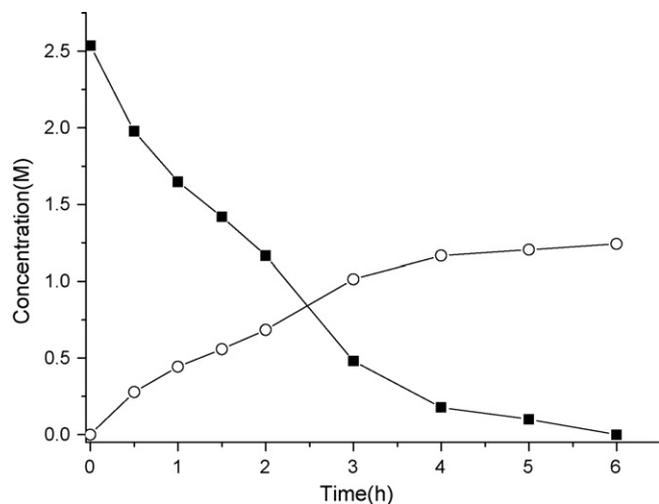
The production rate of azoxybenzene in the oxidation of aniline was also studied (Fig. 3). As shown in the diagram, there was no induction period for this catalyst. It appears that the conversion was fast with more than 80% conversion after 3 h. From this reaction profile, the ratio of the reactant disappearance versus the product formation almost kept constant (2:1). There was no other side product found in this reaction, indicating that the intermediate in this oxidation step was readily converted into the product.

In view of the above results, the catalytic system that renders the best yield in oxidation of aniline into azoxybenzene was applied in the subsequent studies. Various substituted anilines were tested under this reaction conditions and the results are summarized in Table 2. When allowed to react with H_2O_2 via the Si-Co catalyst, substituted anilines afforded the corresponding azoxybenzene in excellent yields. p-Phenylenediamine did undergo coupling to yield a black material, which was presumably polymers (entry 1). It appears that the electronic effect of substituents had little influence on the production of the corresponding azoxybenzene. However, the steric effect of the substituents did affect the reaction. Oxidation of 2,4,6-trimethylaniline offered azoxymesitylene in 92% yield, but the 2,6-diisopropylaniline gave essentially no desired product (entry 4 versus entry 8). This indicates that the catalytic center is sensitive toward the sterically bulkiness of the substrates.

Finally, the stability and activity of the catalyst was tested in the recycle-use experiments. Typically, a mixture of aniline (5 mmol), Si-Co (5 mg) and H_2O_2 (10 mmol) in acetonitrile (1 mL) was heated to 80 °C for 8 h. The mixture was filtered and the catalyst was washed twice with acetone, dried and reused in the further reaction. Over a period of three reaction cycles under the same conditions, no significant loss of activity was observed and the yield for each run was 98%, 97% and 95%, respectively.

In summary, the procedure in this work offers several advantages for the preparation of azoxybenzenes from the corresponding aniline such as low loading of catalyst, mild conditions, high yields, and clean reactions, which make it a useful and attractive methodology for organic synthesis. The simple workup procedure is also beneficial to this method. Although the preparation of the catalyst was nontrivial, it offers information for the future design of new catalysts. Further applications of this catalyst to other transformations are currently under investigation.

Table 1
Results of the oxidation of aniline with H_2O_2 in the presence of Si-Co[a].

Entry	Catalyst	Oxidant	Solvent	T (°C)	t (h)	Conv.[b]	Yield[c]
1	Si-Co	H_2O_2 (10 mmol)	CH_3CN	25	8	26	26
2	Si-Co	H_2O_2 (20 mmol)	CH_3CN	25	8	58[e]	56
3	Si-Co	H_2O_2 (25 mmol)	CH_3CN	25	8	62	62
4	Si-Co	H_2O_2 (10 mmol)	CH_3CN	55	8	78[e]	77
5	Si-Co	H_2O_2 (10 mmol)	CH_3CN	80	6	100	100
6	None	H_2O_2 (10 mmol)	CH_3CN	25	8	10	[f]
7	None	H_2O_2 (10 mmol)	CH_3CN	80	8	60	[f]
8	Si[d] + CoCl$_2$	H_2O_2 (10 mmol)	CH_3CN	25	8	9	9
9	Si-Co	TBHP (10 mmol)	CH_3CN	25	8	0	0
10	Si-Co	H_2O_2 (10 mmol)	CH_3OH	25	8	9	[e]
11	Si-Co	H_2O_2 (10 mmol)	Acetone	25	8	5	5
12	Si-Co	H_2O_2 (10 mmol)	THF	55	8	24	24
13	Si-Co	H_2O_2 (10 mmol)	H_2O	55	8	53	53
14	Si-Co	H_2O_2 (10 mmol)	H_2O	80	8	65	65
15	Si-Co	H_2O_2 (10 mmol)	H_2O	100	8	100	97[g]

[a] Reaction conditions: aniline (5 mmol), catalyst (5 mg) and solvent (1 mL).
[b] Determined by GC analysis.
[c] Amount of azoxybenzene based on NMR yields.
[d] SBA-15 silica (5 mg) and CoCl$_2$·2H$_2$O (0.3 mg) in water (2 mL) were mixed and the solvent was removed under vacuum. The residue was used as the catalyst.
[e] Trace of azobenzene.
[f] A mixture of various products including PhN=NPh and PhNHOH, but major for azobenzene.
[g] Azobenzene (3%) was obtained.

Table 2
Formation of azoxybenzenes via oxidation of anilines[a].

Entry	Anilines	Products	Yield (%)
1	p-Phenylenediamine	Polymer	–
2	4-t-Butyianiline		98
3	4-Methoxyaniline		86
4	2,4,6-Trimethylaniline		92
5	4-Bromoaniline		71
6	4-Nitroaniline		59
7	1-Aminonaphathalene		67
8	2,6-Diisopropylaniline	No reaction	–
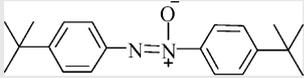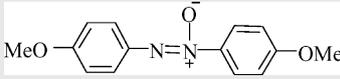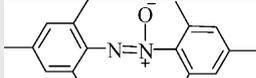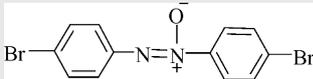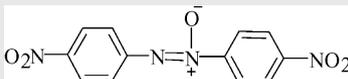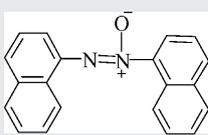
[a] Reaction conditions: aniline compound (5 mmol), H_2O_2 (10 mmol) and Si-Co (5 mg) in CH_3CN at 80 °C.

3. Experimental

3.1. General

All reaction steps for polymerization were performed under a dry nitrogen atmosphere. Dichoromethane was dried with CaH$_2$ and distilled under nitrogen. [CH$_3$(OCH$_2$CH$_2$)$_n$OTs] (**1**) and N[CH$_2$CH$_2$N(CH$_3$)$_2$]$_3$ (Metren) were prepared according to the method reported in the literature [11]. Nuclear magnetic resonance spectra were recorded in CDCl$_3$ on a Bruker AM-300 spectrometer. Infrared spectra were measured on a Nicolet Magna-IR 550 spectrometer (Series-II) as KBr pallets. Gel permeation chromatography (GPC) data were obtained from a Waters Model 590 liquid chromatograph installed with a Lab Alliance RI 2000 detector using THF as eluant (at the rate 1 mL/min) at 40 °C and polystyrene calibration curve for analyses.

3.2. Synthesis and characterization

3.2.1. Preparation of macro-initiator (**2**)

To a mixture of tosylate **1** (21.35 g, 10 mmol) and sodium azide (2.6 g, 40 mmol) in a flask was added acetone (600 mL). The resulting mixture was heated to reflux for 24 h. Upon filtration off the salt, the azido compound was obtained (18.1 g, 88%): ^{1}H NMR (CDCl$_3$) δ 3.61 (176H, s, $-OCH_2CH_2O-$), 3.52 (2H, t, $J = 5$ Hz, $-OCH_2CH_2N_3$), 3.38 (2H, t, $J = 5$ Hz, $-OCH_2CH_2N_3$), 3.35 (3H, s, $-OCH_3$).

The reaction of the obtained azide (20.4 g, 10 mmol) and hydrogen gas (200 psi in a 500-mL autoclave) on Pd/C (200 mg) in 150 mL of ethanol produced the corresponding amine (18.0 g, 89%). ^{1}H NMR δ 3.61 (176H, s, $-OCH_2CH_2O-$), 3.48 (2H, t, $J = 6$ Hz, $-OCH_2CH_2N-$), 3.35 (3H, s, $-OCH_3$), 2.83 (2H, t, $J = 6$ Hz, $-OCH_2CH_2N-$).

2-Bromoisobutyryl bromide (1.36 mL, 11 mmol) was added into a mixture of the amine compound (20.24 g) and triethylamine (10 mL) in anhydrous CH$_2$Cl$_2$ (150 mL) with stirring at 0 °C. Upon addition, the mixture was further stirred at room temperature for 6 h. Water (100 mL) was then added and the organic layer was separated. After concentration, the residue was washed with ice-cooled ether (3× 100 mL) and the desired compound **2** was obtained as white solids (17.7, 82%). ^{1}H NMR δ 3.61 (176H, s, $-OCH_2CH_2O-$), 3.52 (2H, t, $J = 6$ Hz, $-OCH_2CH_2N-$), 3.38 (2H, t, $J = 6$ Hz, $-OCH_2CH_2N-$), 3.35 (3H, s), 1.92 (6H, s, $-C(CH_3)_2$).

3.2.2. Diblock copolymer (EO-MA)

A mixture of **2** (2.1 g) and CuBr (28.6 mg) was placed in a flask sealed with a septum. The flask was evacuated and flashed with nitrogen three times. Methyl acrylate (7.2 mL, 80 mmol) was syringed into the above mixture with stirring. Metren (56 μL, 0.2 mmol) was then added and the polymerization took place immediately. After stirring 10 min, the reaction was quenched by the addition of THF (30 mL). The reaction mixture was filtered through silica gel to remove the catalyst. Upon concentration and re-precipitation in ether/methanol, the obtained copolymer was dried under vacuum overnight (3.5 g). ^{1}H NMR (CDCl$_3$) δ 3.64–3.60 (296H, br), 3.37 (3H, s, $-OCH_3$), 2.29 (40H, br), 2.00–1.30 (80H, br), 1.14 (3H, s, $-C(CH_3)_2$), 1.12 (3H, s, $-C(CH_3)_2$). GPC: $M_N = 4500$, PDI = 1.14.

3.2.3. Modification of copolymer (EO-MA-N)

A mixture of EO-MA (2.0 g) and NH$_2$(CH$_2$)$_3$N$_3$ (5 mL) was heated to 100 °C for 10 h. Excess of azide was removed under vacuum and the residue was dissolved in CH$_2$Cl$_2$. Addition of hexane gave the desired product as white precipitates (2.6 g).

This solid (2.0 g) dissolved in dried THF (10 mL) was slowly added to a solution of PPh$_3$ (1.31 g) in THF (10 mL). The resulting mixture was stirred at room temperature for 10 h. Then water (10 mL) was added. The mixture was heated to reflux for 1 h. After cooling, the organic layer was separated and washed with brine. The crude product was washed with ether (3× 50 mL) to give EO-MA-N as white solids (1.45 g). ^{1}H NMR (CDCl$_3$) δ 3.70–3.60 (296H, br), 3.40 (3H, $-OCH_3$), 3.33 (2H, CH$_2$–N), 2.88 (2H, $-NH-CH_2$), 2.40–1.30 (122H, $-CHCH_2-$), 1.14–1.12 (6H, $-C(CH_3)_2$). FTIR υ (cm^{-1}) (KBr): 3423 (br, N–H), 1746 (vs, C=O), 1673 (vs, CONH).

3.2.4. Cobalt-containing mesoporous silicas (Si-Co)

A mixture of EO-MA-N (0.5 g), CoCl$_2$ (0.12 g), 37% HCl (6.0 g), and Si(OEt)$_4$ (1.5 g) in water (25 g) was stirred at room temperature for 24 h. The obtained mesoporous silicas in 50.0 g water was hydrothermally treated at 100 °C for 24 h. The organic templates were removed by calcinations at 560 °C for 6 h under air, which allowed the cobalt complex to form the metal oxide.

3.2.5. Characterization of Si-Co

The powder X-ray diffraction patterns (XRD) were taken on a Scintag X1 instrument ($\lambda = 0.1326$ nm). The TEM images of mesoporous silicas were recorded on a Hitachi S-7100 transmission electron microscope (TEM) with an operating voltage of 75 keV. The N$_2$ adsorption–desorption isotherms were obtained at 77 K on a Micromeritics ASAP 2010 apparatus, and the pore size distribution was calculated from the adsorption isotherms using the Barrett–Joyner–Halenda (BJH) method.

3.3. Catalysis

A mixture of substrate (5 mmol), H$_2$O$_2$ (37%, 10 mmol), solvent (1 mL) and Si-Co (5 mg) was placed in a 20-mL flask. The solution was stirred at a certain temperature. Upon standing for 1 h, the organic product was separated from the reaction mixture by extraction with dichloromethane (2× 2 mL). The combined organic portions was dried and concentrated. Product analysis was performed by GC and ^{1}H NMR spectroscopic methods, which were all essentially identical to those reported in the literature.

3.3.1. ^{1}H NMR data of products

3.3.1.1. Aazoxybenzene. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.36–7.85 (5H, m, Ar–H), 8.14–8.29 (5H, m, Ar–H) [10b].

3.3.1.2. 4,4′-Di-t-butylazoxybenzene. ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.34 (9H, s), 1.35 (9H, s), 7.20–7.40 (4H, m), 7.90–8.21 (4H, m) [15].

3.3.1.3. 4,4′-Dimethoxyazoxybenzene. ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.85 (6H, s, OMe), 7.0–7.2 (4H, m), 8.15–8.23 (4H, m) [10b].

3.3.1.4. Azoxymesitylene. ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.18 (6H, s), 2.29 (3H, s), 2.35 (3H, s), 2.37 (6H, s), 6.81 (2H, s), 6.90 (2H, s) [16].

3.3.1.5. 4,4′-Dibromoazoxybenzene. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.51 (2 H, d, $J = 6$ Hz), 7.71 (2H, d, $J = 6$ Hz), 8.12 (2H, d, $J = 6$ Hz), 8.32 (2H, d, $J = 6$ Hz) [10b].

3.3.1.6. 4,4′-Dinitroazoxybenzene. ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.35 (4H, br), 8.57 (4H, br) [10b].

3.3.1.7. 1,1′-Aazoxynaphthalene. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.45 (6H, m), 7.89 (5H, m), 8.28 (1H, m), 8.61 (1H, m), 9.2 (1H, m) [10b].

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