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New Co(II) and Cu(II) Phthalocyanine Catalysts Reinforced by Long Alkyl Chains for the Degradation of Organic Pollutants

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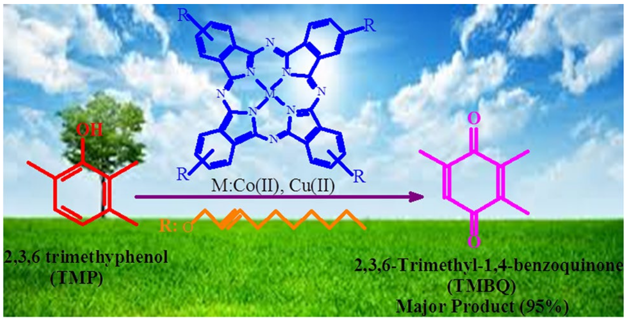
Abstract The need to develop sustainable, low-cost, earth abundant catalyst is becoming paramount for overcoming environmental problems. Toward this goal, new cobalt(II) and copper(II) phthalocyanine complexes used as catalyst for degradation of organic pollutants (such as 2,3-dichlorophenol, 4-methoxyphenol, 4-nitrophenol, 2,3,6-trimethylphenol) with different oxygen source. This catalytic system with these complexes showed high conversion rates for degradation of organic pollutants and could easily be recovered by recycling reactions.

Graphical Abstract



Keywords Phthalocyanine · Cobalt · Copper · Organic pollutants · Degradation

1 Introduction

Environmental problems are normally recounted to waste and toxic organic with inorganic pollutants released in water bodies. The majority of the coloured and uncoloured effluents originated in contaminated waters contain organic dyes and phenolic compounds from textiles, dyestuff, dyeing industries, fertilizers and chemical production industries [1–3]. Phenolic compounds are a major class of environmental pollutants and are potential human carcinogens. They are widely used in the manufacturing processes of plastics, dyes, drugs, pesticides and papers. Their disposal may contaminate soil and water. Because of increasing public health concerns and stricter regulations on treatment and disposal, it becomes more important to develop newer and efficient methods for removing these compounds from wastewaters [4–8] The reported methods for removing phenolics from wastewaters include activated carbon adsorption [9], microbial degradation [10], chemical oxidation [11], corona discharge [12], enzymatic degradation [13], etc. The toxic and bio-resistant organo chlorine compounds in aqueous systems need to be transformed into harmless species. Various abatement techniques including biological, thermal and chemical treatments have been developed in the last few years for the detoxification of organic pollutants [14]. Metallophthalocyanines (MPc) are very stable metal complexes of macrocyclic tetraazaporphyrin. Thanks to their chemical and thermal stability, low cost, easy preparation, metallophthalocyanines have found many applications in medical and industrial areas such as gas and chemical sensors, molecular solar cells, industrial catalytic

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systems, electrochromic display devices, optical switching, nanotechnology and light-emitting devices in recent years [15]. Due to the fact that cobalt and copper phthalocyanines immediately interact with oxidant and transfer oxygen to substrate (such as alcohols, alkenes, thiols, phenols etc.), they are widely used as oxidation catalysts in oxidation process [16–23]. They can oxidize different phenolic compounds to quinones and aldehydes as major product. Selective oxidation of phenol to quinones is the key step in the preparation of many vitamins and valuble synthetic precursors [24].

In this paper, 2-decyn-1-oxi substituted cobalt(II) **4** and copper(II) **5** phthalocyanine have been synthesized. Solubility of phthalocyanines in water or polar solvents can be improve by attaching sulfo [25] or quaternary ammonium groups [26], crown ethers [27], long substituted alkyl [28], alkoxy [29], alkylthio [30], macrocyclic groups [31] peripherally or non-peripherally position on the phthalocyanine ring. Thanks to the long alkyl chain substituent groups, Co(II) and Cu(II) phthalocyanine complexes **4** and **5** can readily dissolve in some polar solvents [32]. Herein, it has been reported that the successfull application of Co(II) and Cu(II) phthalocyanines as oxidation catalysts for oxidation of 2,3-dichlorophenol, 4-methoxyphenol, 4-nitrophenol, 2,3,6-trimethylphenol using with biphasic solvent system. The catalyst and the oxidation products were easily recovered and reused in the reaction media.

2 Experimental

2.1 Materials

The used materials, equipments and catalysis procedure were supplied as supplementary information.

2.2 Synthesis

2.2.1 Synthesis of 4-(dec-2-yn-1-yloxy)phthalonitrile (3)

4-Nitrophthalonitrile (**2**) (2.24 g, 12.94 mmol) was dissolved in 10 mL dry DMF under N_2 atmosphere, and of 2-decyn-1-ol (**1**) (2.0 g, 12.94 mmol) added to mixture. After stirring for 30 min at 60 °C, finely ground anhydrous K_2CO_3 (5.357 g, 38.82 mmol) was added portion wise within 2 h. The reaction mixture was stirred under N_2 at 60 °C for 3 days. At the end of this time, the reaction mixture was poured into ice-water and stirred at room temperature for 3 h to yield a crude product. The mixture was filtered and dried in vacuum over P_2O_5 for 4 h and recystallized from ethanol to give bright brown crystalline powder. Yield: 2.45 g (72%). mp: 42–43 °C. Anal.calc. for $C_{18}H_{20}N_2O$ IR (KBr pellet), ν_{max}/cm^{-1}: 3086, 3046 (Ar–H), 2922, 2963, 2855 (Aliph. C–H), 2231 (C≡N), 1667–1596 (C–O), 1505, 1486, 1473, 1458, 1349, 1285, 1255, 1211, 1169, 1152, 1086, 1035, 969, 944, 907, 851, 839, 754, 742, 713. ^{1}H-NMR. ($CDCl_3$), (δ:ppm): 7.90 (d, 7.0, 1H, Ar–H), 7.45 (m, 7.2, 2H, Ar–H), 4.79 (d, 6.8, 2H, CH_2-O), 2.20–2.14 (t, 6.4, 2H, CH_2-C), 1.48–1.33 (m, 10H, $–CH_2$), 0.90–0.81 (t, 6.6, 3H, $–CH_3$). ^{13}C-NMR. ($CDCl_3$), (δ:ppm): 161.88(C_1), 135.22(C_3), 122.70(C_2), 122.38(C_6), 120.43(C_5), 117.30 (C_7≡N), 112.54 (C_8≡N), 106.46(C_4), 88.64(C_{11}), 76.81(C_{10}), 56.96(C_9), 32.10(C_{16}), 30.04(C_{15}), 29.85(C_{14}), 29.12(C_{13}), 22.90(C_{17}), 19.08(C_{12}), 14.83(C_{18}). MALDI-TOF-MS, (m/z): Calculated: 280.36; Found: 298.40 $[M+H_2O]^+$ $C_{18}H_{20}N_2O$: calcd. C 77.11; H 7.19; N 9.99%; found: C 77.40; H 7.10; N 10.01.

*2.2.2 General Procedure of Metal Phthalocyanines **4–5***

To give the metal phthalocyanies, the mixture of phthalonitrile compound 3 (0.5 g, 1.78 mmol), the related anhydrous metal salt ($CoCl_2$) (57.61 mg, 0.445 mmol) for compound **4**, $CuCl_2$ (59.87 mg, 0.445 mmol) for compound **5** and two drops of DBU was heated at 160 °C in dry n-pentanol (3 mL) in a sealead tube, and stirred for 24 h. At the end of the reaction, green product was precipitated by addition of ethanol (20 mL) and filtered off. Along 2 h, the green solid product was refluxed with ethanol (30 mL), filtered off again and washed with hot ethanol, distilled water and diethyl ether. After drying under vacuum, the product was purified on basic alumina column with chloroform–methanol (92:8) for compound **4**, (95:5) for compound **5** solvent system as eluent.

2.2.2.1 Synthesis of Cobalt(II) phthalocyanine (4) Yield: 250 mg (47%). Mp > 300 °C. Anal.calc. for $C_{72}H_{80}O_4N_8Co$ FT-IR ν_{max}/cm^{-1} (KBr pellet): 3076, 3009 (Ar–H), 2986, 2953, 2841 (Aliph. C–H), 1720, 1612, 1508, 1461, 1427, 1393, 1336, 1267, 1216, 1149, 1086, 1035, 994, 944, 816, 771, 741, 713. UV–Vis ($CHCl_3$): λ_{max}, nm (log ε): 674 (4.88), 609 (4.55), 332 (4.75). MALDI-TOF-MS, (m/z): Calculated: 1179.57; Found:1181.38 $[M+H]^+$ $C_{72}H_{80}O_4N_8Co$: calcd. C 77.11; H 7.19; N 9.99%; found: C 77.56; H 7.21; N 10.03.

2.2.2.2 Synthesis of Copper(II) phthalocyanine (5) Yield: 240 mg (45%). Mp > 300 °C. Anal.calc. for $C_{72}H_{80}O_4N_8Cu$ FT-IR ν_{max}/cm^{-1} (KBr pellet): 3081, 3022 (Ar–H), 2974, 2943, 2840 (Aliph. C–H), 1750, 1602, 1510, 1442, 1437, 1373, 1355, 1287, 1213, 1156, 1091, 1042, 997, 939, 835, 787, 751, 726. UV–Vis ($CHCl_3$): λ_{max}, nm (log ε): 686 (5.02), 615 (4.38), 330 (4.68). MALDI-TOF-MS, (m/z): Calculated:1184.17; Found:1185.20 $[M+H]^+$ $C_{72}H_{80}O_4N_8Cu$: calcd. C 73.03; H 6.81; N 9.46%; found: C 73.00; H6.82; N 9.42.

3 Results and Discussion

3.1 Synthesis and Characterization

The synthetic pathways for new cobalt(II) and copper(II) phthalocyanine compounds were outlined in Fig. 1. The substituted phthalonitrile compound **3** was obtained by the aromatic nucleophilic substitution reaction between **2** and **1**. Cobalt(II) and Copper(II) phthalocyanines **4** and **5** were purified by column chromatography on basic alumina using [($CHCl_3$:CH_3OH, 92:8) or ($CHCl_3$:CH_3OH, 95:5)] solvent mixtures as eluents, respectively. The structures of the target compounds were confirmed using UV–Vis, IR, ^1H-NMR, ^{13}C-NMR, mass (MALDI-TOF technique) spectroscopic data and elemental analysis.

In the IR spectrum of compound **3**, stretching vibrations at 2231 cm^{-1} for C≡N groups, at 3086 and 3046 cm^{-1} for aromatic CH groups, at 2922–2855cm^{-1} for aliphatic CH groups appeared at expected frequencies. In the ^1H NMR spectrum of compound **3**, the aromatic protons were obtained at 7.90 (d), 7.45 (m) ppm and aliphatic protons were obtained at 4.79 (d), 2.20–2.14 (t), 1.48–1.33 (m),

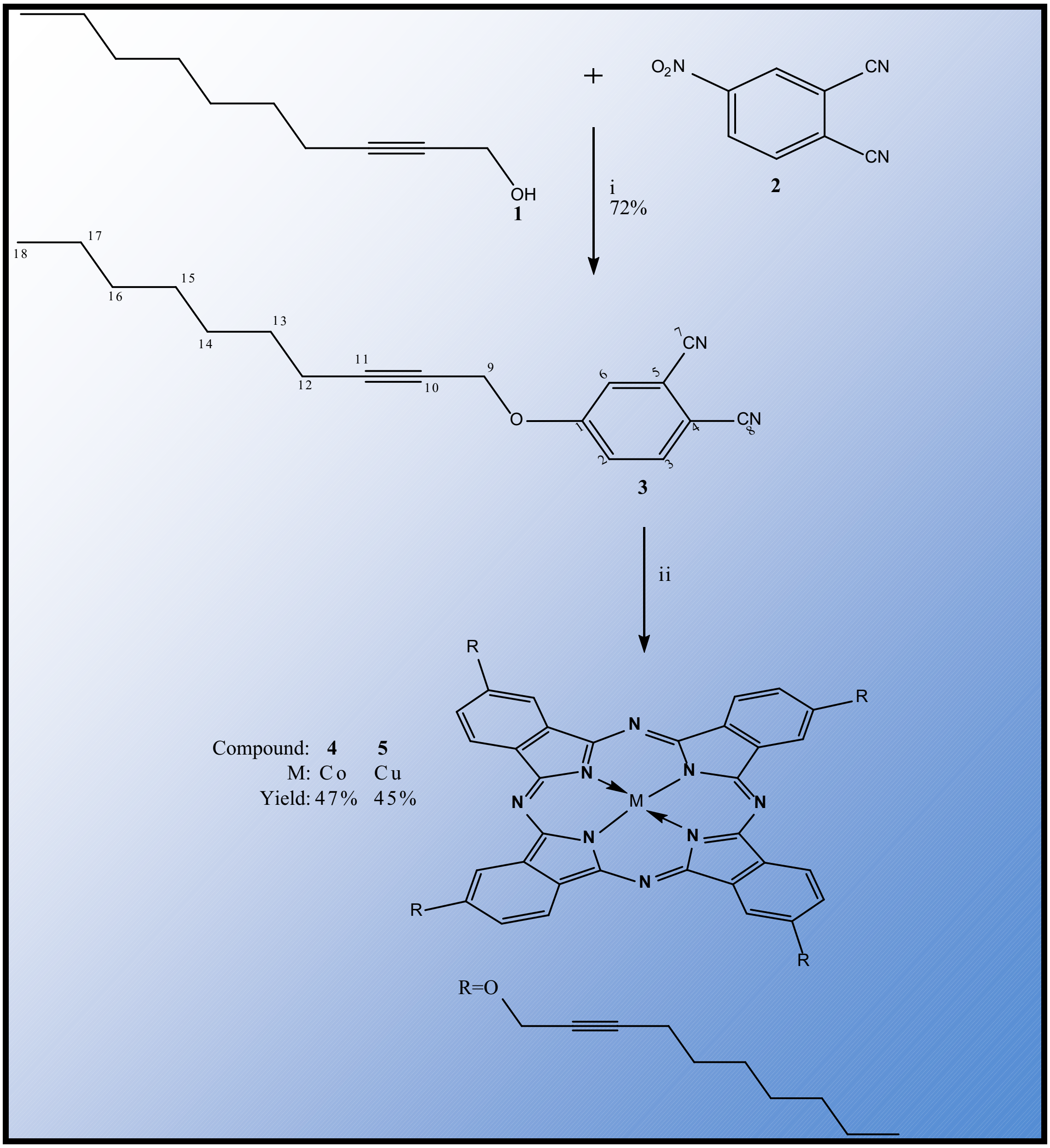


Fig. 1 The synthetic route of the phthalonitrile, cobalt phthalocyanine and copper phthalocyanine. Reagents and conditions: (i) dry DMF, K_2CO_3, 60 °C, 96 h; (ii) n-pentanol, DBU, 160 °C, $CoCl_2$, $CuCl_2$

0.90–0.81 (t) ppm. The ^{13}C-NMR spectra of compound **3** indicated carbon atoms between at 161.88–14.83 ppm. The nitrile carbon atoms for compound **3** were also observed at 117.30 and 112.54 ppm. In the mass spectum of compound **3**, the presence of molecular ion peak at $m/z=298.40$ $[M+H_2O]^+$, confirmed the proposed structures. The results of the elemental analysis also confirmed the structure of compound **3**. The cyclotetramerization of the phthalonitrile compound **3** to the cobalt(II) and copper(II) phthalocyanine **4** and **5** can be seen clearly by the disappearance of the peaks at 2231 cm^{-1} belonging to the C≡N vibrations. The IR spectra of **4** and **5** showed similar characteristics. The NMR spectra of peripherally tetra-substituted cobalt(II) and copper(II) phthalocyanines **4** and **5** were not be able to take into precluded owing to their paramagnetic nature [33]. The mass spectra of compounds **4** and **5**, which showed peaks at $m/z=1181.38$ $[M+H]^+$and 1185.20 $[M+H]^+$respectively support the proposed formula for these compounds. The results of the elemental analysis also confirmed the structure of complexes **4** and **5**.

The electronic spectra of the phthalocyanines have two strong absorption bands in UV/Vis spectroscopy. One of them is in the visible region at 600–700 nm (Q Band) due to electronic transitions from π-highest occupied molecular orbital (HOMO) to π^*-lowest unoccupied molecular orbital (LUMO) energy levels, and the other one is in the UV region at about 300–500 nm (B or Soret Band) due to transitions from deeper π-HOMO and π^*-LUMO energy levels [34]. The Q-band of the phthalocyanines is more intense than Soret band. While the Q bands of the metal-free phthalocyanines are splitted two bands, owing to D_{2h} symmetry and the lifting of degeneracy of the LUMO level, as Q_x, Q_y bands that of metallophthalocyanines are observed as a single band owing to D_{4h} symmetry [35]. The Q-band absorptions of π–π^* transition for both phthalocyanines in chloroform were observed as a single band of high intensity at 674 nm for **4**, 686 nm for **5**. There was also a shoulder at the slightly higher energy side of the Q band for each phthalocyanine. B band absorptions of the metallophthalocyanines **4–5** were observed at 330, 332 nm respectively (Fig. 2).

3.2 Catalytic Studies

The main product as 2,3,6-trimethyl-1,4-benzoquinone, the key intermediate in the synthesis of vitamin E, the side product as 2,2′,3,3′,5,5′-hexamethyl-4,4′-biphenyldiol (BP) were determined in the oxidation of 2,3,6 trimethyphenol oxidation reaction (Fig. 3). These preliminary results exhibited that these complexes could facilitate the oxidation of 2,3,6 trimethylphenol and serve as selective and efficient catalyst. Hexane-acetonitrile (1:1) solvent mixture is used in all oxidation reactions to form biphasic reaction medium. All substrate, major products, catalysts within the oxidation processes are summarized in Table 1. According the results of this table, both catalysts showed the highest activity producing 2,3,6-trimethyl-1,4-benzoquinone as major product in 2,3,6-trimethylphenol oxidation reaction.

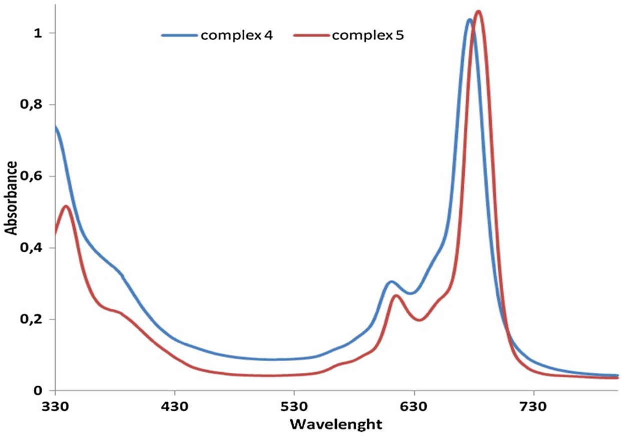


Fig. 2 UV–Vis spectrum of complex 4 and 5 in chloroform

Then, optimization of the reaction conditions were carried out by selectively evaluating effects of different 2,3,6-trimethylphenol-to-catalysts molar ratios, oxidant-to-catalysts molar ratios, the oxidant and temperature used. Additionally, in the blank reactions (without catalysts or oxidants) there were no product detectable. It is proved that presence of the catalyst and oxidant are essential for the oxidation (Table 2). As the other parameters were kept constant, the molar ratio was carried out in the range of 500–1500 to determine the influence of substrate to metal ions. As we expected, the reaction rate increased with decreasing of the substrate/catalyst molar ratio (Table 2). Substrate/catalyst ratio on the oxidation course gave same main product (TMBQ) with TON and TOF values (493 for **4**, 389 for **5** and 164 for **4**, 129 for **5**).

To determine oxygen source effect, H_2O_2, m-CPBA, TBHP and air oxygen were used as oxidant. The results in Table 2 show that TBHP is the best oxidant for 2,3,6-trimethylphenoloxidation in the presence of complex **4** and **5**. Moreover, H_2O_2 and m-CPBA can serve as an oxidant but low conversion for both complexes. Adding H_2O_2 or m-CPBA in the reaction media, the reaction color changed from blue to brown. This clue explains that complex **4** and **5** was degraded immediately with H_2O_2 or m-CPBA [36]. The results of studies for complex **4** and **5** using with air oxygen show that there is no formation of products during the oxidation process. The another important parameter is oxidant/catalyst ratio to find the optimal conditions of 2,3,6-trimethylphenol oxidation. When the increasing oxidant/catalyst ratio from 300/1 to 800/1, the rate of the reaction increased. In contrast, while the catalytic oxidation was

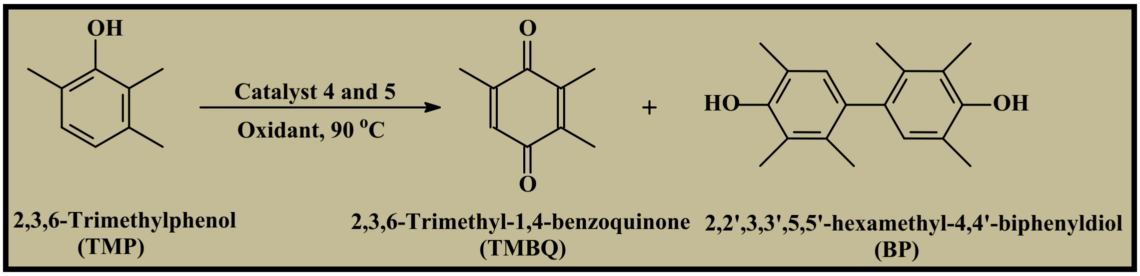
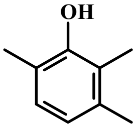
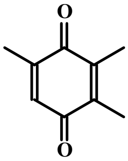
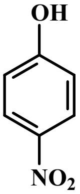
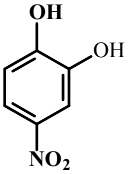
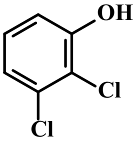
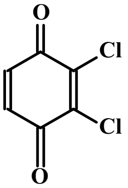
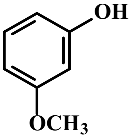
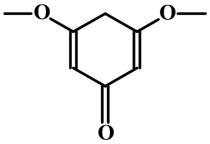


Fig. 3 The oxidation products of 2,3,6-trimethylphenol

Table 1 Oxidation of substituted phenols catalyzed by complex 4 and 5 using biphasic solvent system

Substrate	Major product	Total conversion (%)		Product selectivity (%)		TON		TOF (h^{-1})	
		4	5	4	5	4	5	4	5
		99	78	95	89	493	389	164	129
		68	55	85	69	337	274	112	91
		73	70	59	40	364	349	121	116
		45	30	97	50	225	149	74	49

TON = mole of product/mole of catalyst

TOF = mole of product/mole of catalyst × time

Conversion was determined by GC

Catalyst/substrate/oxidant ratio = 1/300/500, reaction time = 3 h

processing from 800/1 to 1200/1, the conversion inclined to decrasing. At this stage, it is possible that the coordination around the cobalt and copper ion can change and produce inactive intermediate species [37]. The results in Table 2 show that as the reaction temperature was upgraded, the catalytic activity of complex **4** and **5** increased. When the temperature was reduced from 90 to 25 °C, the total conversion was changed from 99 to 45% for complex **4** and 78–38% for complex **5**, therefore 90 °C is the optimum temperature of 2,3,6-trimethylphenol oxidation with TBHP in 3 h.

Recyclability is an important and essential feature for any catalyst to be considered in large-scale catalytic reactions. As shown in Fig. 4, after completion of the oxidation

Table 2 Selective oxidation of 2,3,6-trimethylphenol with catalysts 4 and 5 using different oxidant and temperature

Subs./Ox./Cat	Oxidant	Temperature (°C)	Conversion (%)		Selectivity[a] (%)		TON		TOF (h^{-1})	
			4	5	4	5	4	5	4	5
500/300/1	TBHP	90	48	36	61	58	190	107	63	36
500/500/1	TBHP	90	68	57	58	57	339	284	113	94
800/500/1	TBHP	90	70	62	82	66	558	494	186	164
1200/500/1	TBHP	90	75	68	77	72	897	814	299	271
1500/500/1	TBHP	90	83	71	75	69	1242	1062	414	354
500/800/1	TBHP	90	99	78	95	89	493	389	164	129
500/1000/1	TBHP	90	74	52	76	66	369	259	123	86
500/1200/1	TBHP	90	49	33	68	52	244	164	81	55
500/800/1	m-CPBA	90	34	21	78	60	169	104	123	35
500/800/1	H_2O_2	90	67	47	88	85	334	234	111	78
500/800/1	Air oxygen	90	–	–	–	–	–	–	–	–
500/800/1	TBHP	75	88	72	80	80	438	359	146	119
500/800/1	TBHP	50	58	47	59	56	289	234	96	78
500/800/1	TBHP	25	45	38	55	49	224	189	74	63
300/500/free cat	TBHP	90	–	7	–	–	–	–	–	–
300/free ox./1	TBHP	90	–	–	–	–	–	–	–	–

TON = mole of product/mole of catalyst

TOF = mole of product/mole of catalyst × time

Conversion was determined by GC

Reaction conditions: 500/800/1: 2.04×10^{-3} mol/3.27×10^{-3} mol/ 4.09×10^{-6} mol and solvent mixture (hegzane: acetonitrile) (0.01 L)

[a]Selectivity of TMBQ reaction time = 3 h

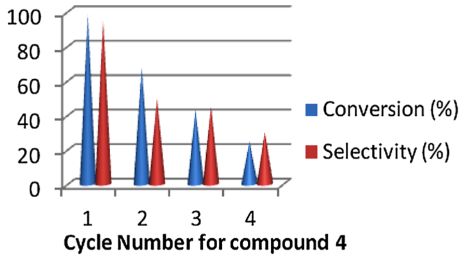


Fig. 4 Recycle experiments of compound 4 on oxidation of 2,3,6-trimethyphenol. Reaction conditions: 2.04×10^{-3} mol 2,3,6-trimethylphenol, 3.27×10^{-3} mol TBHP, 4.09×10^{-6} mol compound 4 and solvent mixture (hegzane:acetonitrile) (0.01 L)

reaction, the catalyst can easily be separated from the reaction mixture. The recovered catalyst was re-activated by adding CH_2Cl_2 three times and further reused directly in a subsequent oxidation of 2,3,6-trimethylphenol reaction. Oxidation products of 2,3,6-trimethylphenol from the first cycle were exracted and the reaction was going on 10 h. GC analysis indicated less than 8% conversion of 2,3,6-trimethylphenol after the fourth cycle with complex **4** and second cycle with complex **5** (Fig. 4). We observed after each cyclic experiment, the conversion of 2,3,6-trimethylphenol decreased substantially. The fast deactivation of catalysts was due to the oxidative degradation of catalysts in the presence of TBHP. Moreover, the degradation of the catalysts was also evidenced by lighter blue solutions after each cycle. We also found that there was almost no TBHP remaining in the reaction medium at the end of reactions in which the number of initial moles of TBHP exceeded the number of initial moles of 2,3,6-trimethylphenol. This finding indicates that some unproductive decomposition of TBHP by the catalyst and/or degradation of catalysts by TBHP occurred [36].

4 Conclusion

As a result, 4-(dec-2-yn-1-yloxy)phthalonitrile **3**, Co(II) and Cu(II) phthalocyanines **4** and **5** were successfully synthesized with the spectral data (UV–Vis, IR, ^{1}H-NMR, ^{13}C-NMR, MS spectroscopic data, elemental analysis). 2,3,6-trimethylphenol oxidation reactions are catalyzed by both catalysts with high conversion and selectivity among the all substrates. Co(II) phthalocyanine shows excellent catalytic activity on 2,3,6-trimethylphenol oxidation with high TON and TOF values in 3 h. The optimal conditions are deteremined in 2,3,6-trimethylphenol oxidation with catalyst **4** and **5**. Converting from environmentally harmfull phenolic compounds into less harmfull oxidation products by Co(II) and Cu(II) phthalocyanines makes this study attractive. These catalytic works are feasible, time-saving in terms of procedure and determined the best oxidation conditions with high TON and TOF values.

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