

Phthalocyanine-based catalysts

Compiled by Mohammad Dashteh

Mohammad Dashteh was born in 1994 in Dashteh/ Hamedan, Iran. Having graduated in the field of Pure Chemistry (2016) from Bu-Ali Sina University, Hamedan, Iran, he continued his M.Sc. in 2018 in Organic Chemistry under the supervision of Professor Mohammad Ali Zolfigol. He is currently working towards his Ph.D. under the supervision of Professor Mohammad Ali Zolfigol and Professor Ardeshir Khazaei in the department of chemistry at Bu-Ali Sina University, Hamedan, Iran. His research interest is the design, synthesis, and characterization of task-specific biological-based catalysts and their applications in organic transformations.

Faculty of Chemistry, Bu-Ali Sina University, Hamedan 6517838683, Iran.

E-mail: mohammaddashteh1994@gmail.com



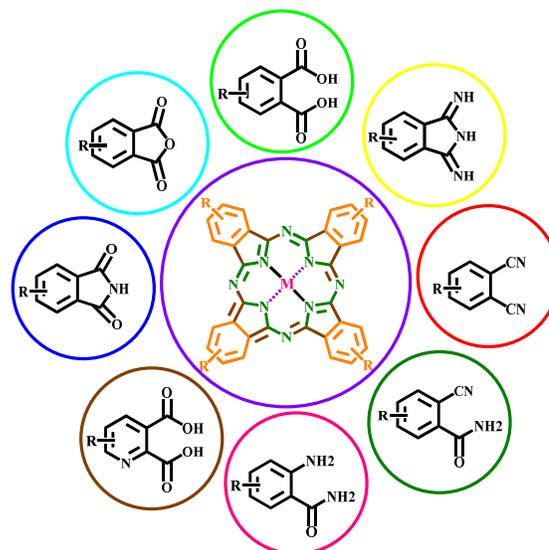
This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

Introduction

Literature surveys with keyword of phthalocyanine at the title of the published papers shows that, 240 reviews and books have been published up to now. This data is showing that the phthalocyanines (Pcs) have great demand in the chemistry and chemical industries. PCs are usually in color because of the intense transition-related to the planar heteroaromatic conjugation system. Thus, due to their broad applications in many fields, Pcs have been studied in detail in varied area of science including photosensitizers, semiconductors, dyes and pigment, solar cells, for optical data storage, as carrier generation material in the near-IR device and others [1]. Pcs have found a varied range of applications in the part of material science because of their different optical and electrical properties as well as their thermal stability [2]. Therefore, metal Pcs as macrocyclic complex are accessible, stable and cost-effective biomimetic oxidation catalysts which generally are used in organic reactions. Among applied metal-center Pcs, vanadium oxide, cobalt, and iron are unique. Scheme 1 displays the various methods for the synthesis of Pcs.

Pcs are the second most important class of colorant, and copper Pcs is the single largest-volume colorant sold. Traditional uses of Pcs colorants are as blue and

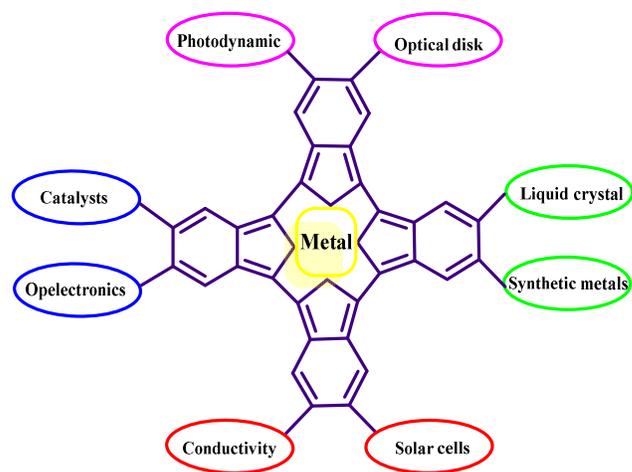
green pigments for automotive paints and printing inks and as blue/cyan dyes for textiles and paper. Pcs have also found extensive use in many of the modern high technologies, e.g. as cyan dyes for ink jet printing, in electrophotography as charge generation materials for laser printers and as colorants for cyan toners. In the visible region, Pcs are limited to blue, cyan and green colors.



Scheme 1. Various methods for the synthesis of Pcs.

The properties and effects of these infrared-absorbing Pcs are diverse and cover many critical hi-tech. However, their absorption may be extended into the near-infrared and by suitable chemical engineering, it is possible to fingerprint the 700-1000 nm region. applications, including photodynamic therapy, optical data storage, reverse saturable absorbers, and solar screens [3].

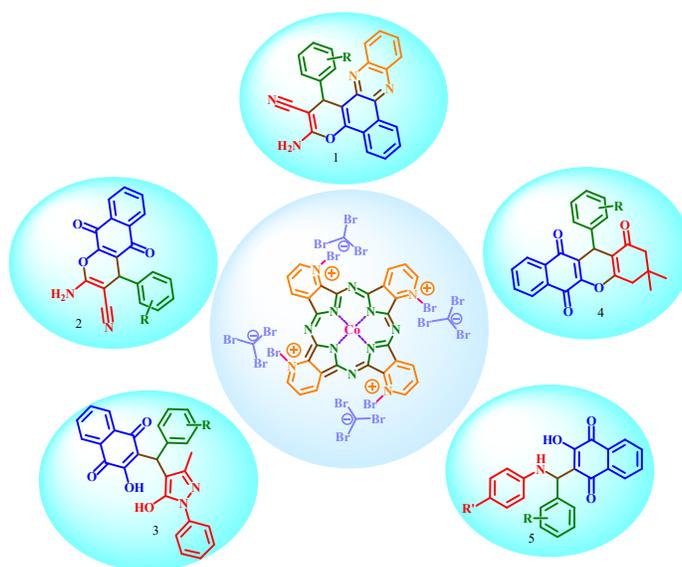
In this spotlight as a mini-review, it has been attempted to review the catalytic properties and application of Pcs in various industries. Several significant applications of Pcs have been studied in numerous scientific fields (Scheme 2). Up to now, any evidences has not been reported for serious toxicity or carcinogenicity of the Pcs compound [4].



Scheme 2. Unique applications of Pcs.

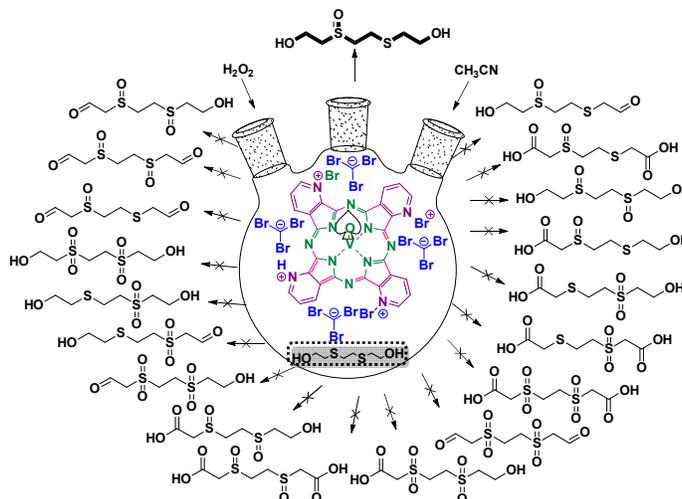
Abstracts

(A) A good range of henna-based compounds have been synthesized by applying nano cobalt phthalocyanine like molten salt (tetra-2,3-pyridiniumporphyrinato cobalt tribromomethanide) $[\text{Co}(\text{TPPABr})]\text{CBr}_3$ as an efficient, recyclable and thermally stable heterogeneous catalyst [5].

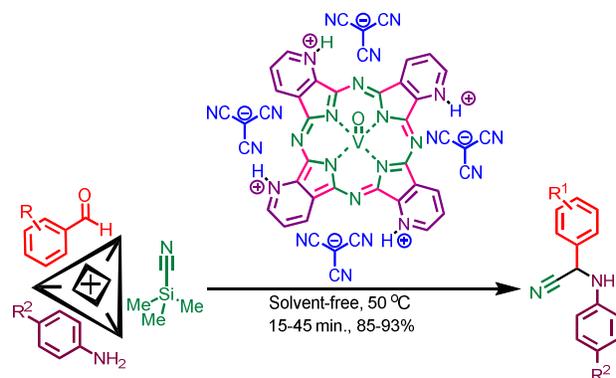


Reaction condition for the synthesis of
1: $\text{C}_2\text{H}_5\text{OH}$, Reflux, cat(20mg); 2: H_2O , Reflux, Cat(10mg); 3: H_2O , Reflux, Cat(10mg); 4: Solvent-free, r.t., Cat(20mg); 5: Solvent-free, r.t., Cat(5mg)

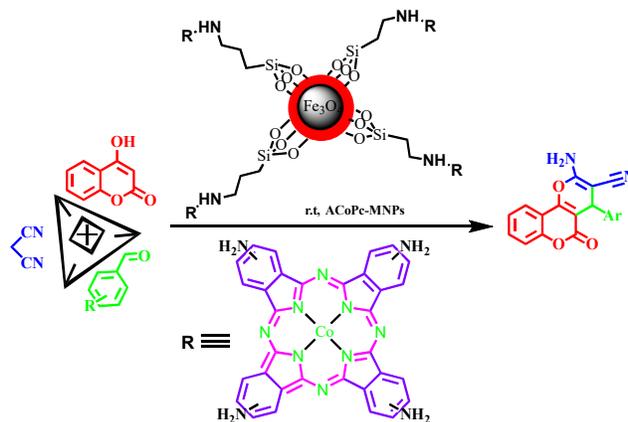
(B) In continued, Chemo and homoselective reaction are great interest in chemical process [6, 7]. The reported pyridiniumporphyrinato oxovanadium tribromomethanide by safaiee et al., acts as an excellent catalyst has been used for the chemo and homoselective oxidation of sulfides and benzylic alcohols [8].



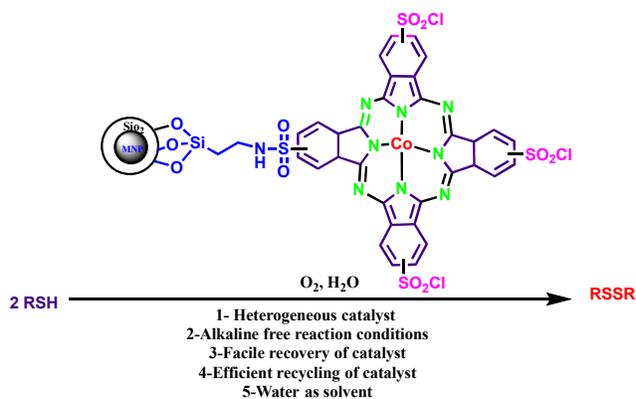
(C) Vanadium surface-free phthalocyanine-based molten salt namely, tetra-2,3 pyridinium porphyrinato-oxovanadium tricyanomethanide, $\{[\text{VO}(\text{TPPA})][\text{C}(\text{CN})_3]_4\}$, was synthesized by Zolfigol et al., and used as a nanocatalyst for the Strecker synthesis of α -aminonitriles. This catalyst was recovered and reused [9].



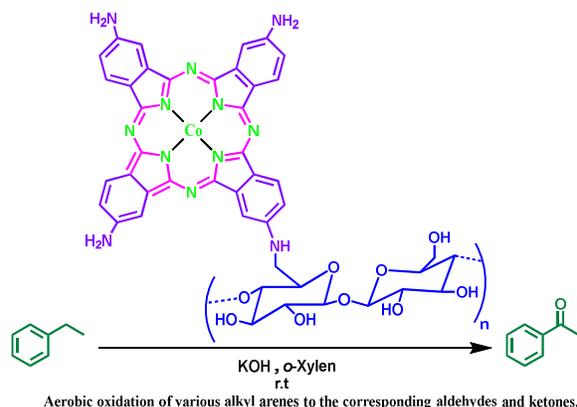
(D) Also, an efficient procedure has been described for the synthesis of magnetic nanoparticles bearing amino cobalt phthalocyanine tags (ACoPc-MNPs). Then, the described catalytic system has been used for the one-pot preparation of tetrahydrobenzo[*b*]pyrans with suitable yields [10].



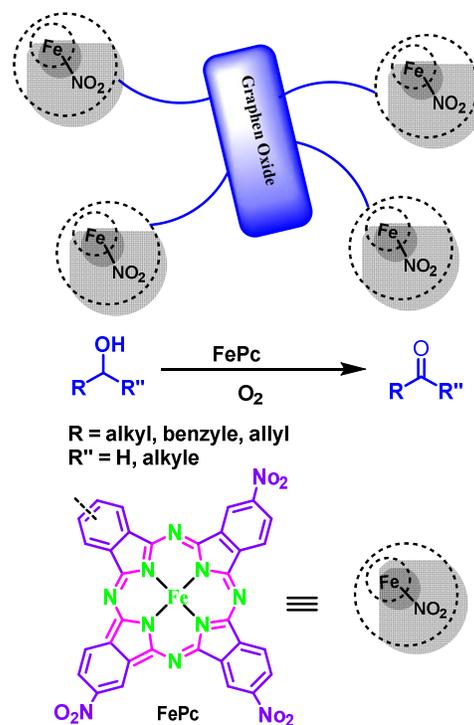
(E) In 2014, an efficient magnetic silica bead functionalized with cobalt phthalocyanine namely, CoPcS@ASMNP, has been designed, synthesized, and used for the oxidation of mercaptans in an alkali-free aqueous medium. Also, the catalyst shows the appropriate potential of recycling and reusing [11].



(F) In another investigation, cobalt (II) phthalocyanines covalently anchored to cellulose has been used as a stable and efficient catalyst for the aerobic oxidation of alkyl arenes and alcohols [12].



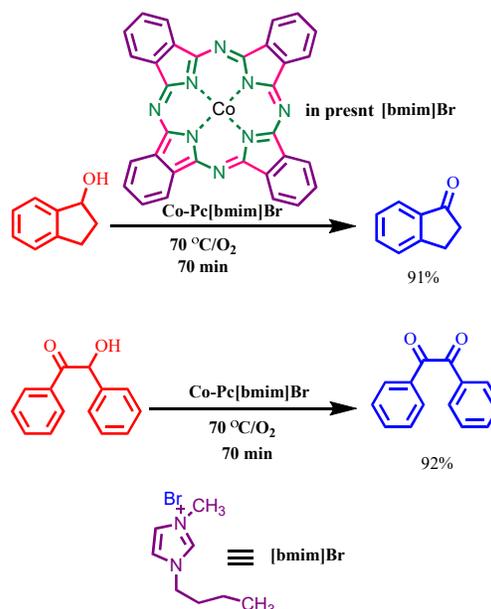
(G) Highly active catalyst based on iron phthalocyanine covalently supported on graphene oxide nanosheets has been synthesized, which included 12% w/w FePc as active phase. The synthesized catalyst has been used for the selective oxidation of numerous alcohols to the corresponding aldehyde and ketone derivatives by molecular oxygen under eco-friendly conditions [13].



(H) In a separate study, the first silica-supported cobalt (II) tetrasulfophthalocyanine was used as a catalyst for the aerobic oxidation of thiols to disulfides at room temperature under solvent-free conditions [14].



(I) In 2008, Shaabani and co-workers, reported an aerobic oxidation methodology for alkyl arenes and alcohols in the presence of cobalt(II)phthalocyanine and 1-butyl-3-methyl-imidazolium bromide as a novel catalytic system [15].



References

- [1] I. Özçeşmeci, Y. Yerli, A. I. Okur, A. Gul. *Inorg. Chem. Commun.* 12 (2009) 625-627.
- [2] J. Alzeer, P. J. Roth, N.W. Luedtk. *Chem. Comm.* 15 (2009) 1970-1971.
- [3] P. Gregory. *J. Porphyr. Phthalocyanines* 4 (2000) 432-437.
- [4] Löbber, G. *Phthalocyanines, Ullmann's Encyclopedia of Industrial Chemistry*, Wiley, 2000.
- [5] M. Dashteh, M. Safaiee, S. Baghery, M. A. Zolfigol. *Appl. Organomet. Chem.* 33 (2019) 1-14.
- [6] Z. Dehbanipour, M. Mohgadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork. *Appl. Organomet. Chem.* 32 (2018) e4436.
- [7] A. Hasaninejad, G. Chehardoli, M. A. Zolfigol, A. Abdoli. *Synlett.* 2 (2011) 271-280.
- [8] M. Safaiee, M. Moeinimehr, M. A. Zolfigol. *Polyhedron* 170 (2019) 138-150.
- [9] S. Baghery, M.A. Zolfigol, M. Safaiee, D.A. Alonso, A. Khoshnood, *Appl. Organometal. Chem.* 31 (2017) e3775.
- [10] M.A. Zolfigol, M. Safaiee, N. Bahrami-Nejad. *New J. Chem.* 40 (2016) 5071-5079.
- [11] G. Singh, P. K. Ganguly, S.K. Jain. *RSC Adv.* 4 (2014) 29124-29130.
- [12] A. Shaabani, S. Keshipor, M. Hamidzad, S. Shaabani. *J. Mol. Catal. A: Chem.* 395 (2014) 494-499.
- [13] M. Mahyari, A. Shaabani. *Appl. Catal. A* 469 (2014) 524-531.
- [14] A. Shaabani, N. Safari, S. Shoghpor, A. H. Rezayan. *Montash. Chem.* 139 (2008) 613-615.
- [15] A. Shaabani, E. Farhang, A. Rahmani. *Appl. Catal. A* 338 (2008) 14-19.