Tetrahedron Letters 54 (2013) 45–48

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Synthesis and characterization of new metallophthalocyanines bearing highly substituted imidazoles

Ali Reza Karimi *, Fahimeh Bayat

Department of Chemistry, Faculty of Science, Arak University, Arak 38156-8-8349, Iran

ARTICLE INFO

Article history:
Received 5 June 2012
Revised 3 October 2012
Accepted 18 October 2012
Available online 24 October 2012

Keywords:
Soluble metallophthalocyanine
Highly substituted imidazole
Aggregation
Microwave synthesis

ABSTRACT

New mono-nuclear metallophthalocyanines (M = Co, Cu, Ni, and Zn) I–V bearing highly substituted imidazole moieties at peripheral positions have been synthesized from derivatives of 4-[4-(2,4,5-triphenyl-1*H*-imidazol-1-yl)phenoxy]phthalonitrile at reflux temperature. These complexes have been characterized by UV/Vis, FT-IR, ^{1}H NMR, MALDI-TOF mass spectrometry, and thermogravimetric analysis. The aggregation behavior of these complexes was investigated under different conditions. Phthalocyanines I, III, IV, and V show monomeric behavior in solution and phthalocyanine V has the highest molar extinction coefficient in the visible region.

Phthalocyanines (Pcs) have attracted significant interest because of their potential applications in fields such as optical disks,[1] photodynamic therapy (PDT),[2] gas sensing,[3] liquid crystals,[4] laser dyes,[5] electronic displays,[6] and semiconducting devices.[7]

The process of self-assembly which is driven by π–π stacking interactions causes a limitation in the use of phthalocyanines in areas such as optics and PDT.[8] Organo-soluble phthalocyanines are therefore important and potentially useful materials. Insolubility can be overcome by introducing bulky substituents onto the peripheral positions of the ring system.[9]

Imidazoles are an important class of heterocyclic system because of their interesting biological effects such as herbicidal,[10] anti-inflammatory,[11] antibacterial,[12] antitumor,[13] and analgesic.[14] In particular, 4,5-diaryl substituted imidazoles are considered as potent inhibitors of p38 MAP kinase.[15] Highly substituted imidazoles can be used as light-sensitive materials in photography,[16] and as fungicides,[17] plant growth regulators,[18] and other types of therapeutic agents.

Introducing imidazole or benzimidazole moieties into phthalocyanines may have a profound effect on their applications in electron transfer processes.[19]

Encouraged by this information and due to our interest in the synthesis of imidazoles[20] and Pcs,[21] herein, we report the preparation of new phthalocyanines (Pcs) containing highly substituted imidazoles (Scheme 1). Moreover, the soluble Pcs synthesized in this study may demonstrate new biological, optical, and electrical properties.

Initially, the preparation of highly substituted imidazoles with one hydroxyl group was undertaken. 1,2,4,5-Substituted imidazoles $\mathbf{A_1}$ and $\mathbf{A_2}$ were prepared via one-pot, four-component condensation reactions of benzil (**1**), 4-aminophenol (**2**), an aldehyde, and ammonium acetate using the heteropolyacid, $H_6P_2W_{18}O_{62}{\cdot}24H_2O$ (WD) supported on silica (WD/SiO_2) as the catalyst.[20a] The formation of compounds $\mathbf{A_1}$ and $\mathbf{A_2}$ was confirmed by the presence of OH signals and the disappearance of C=O signals in their analytical spectra (IR, NMR).

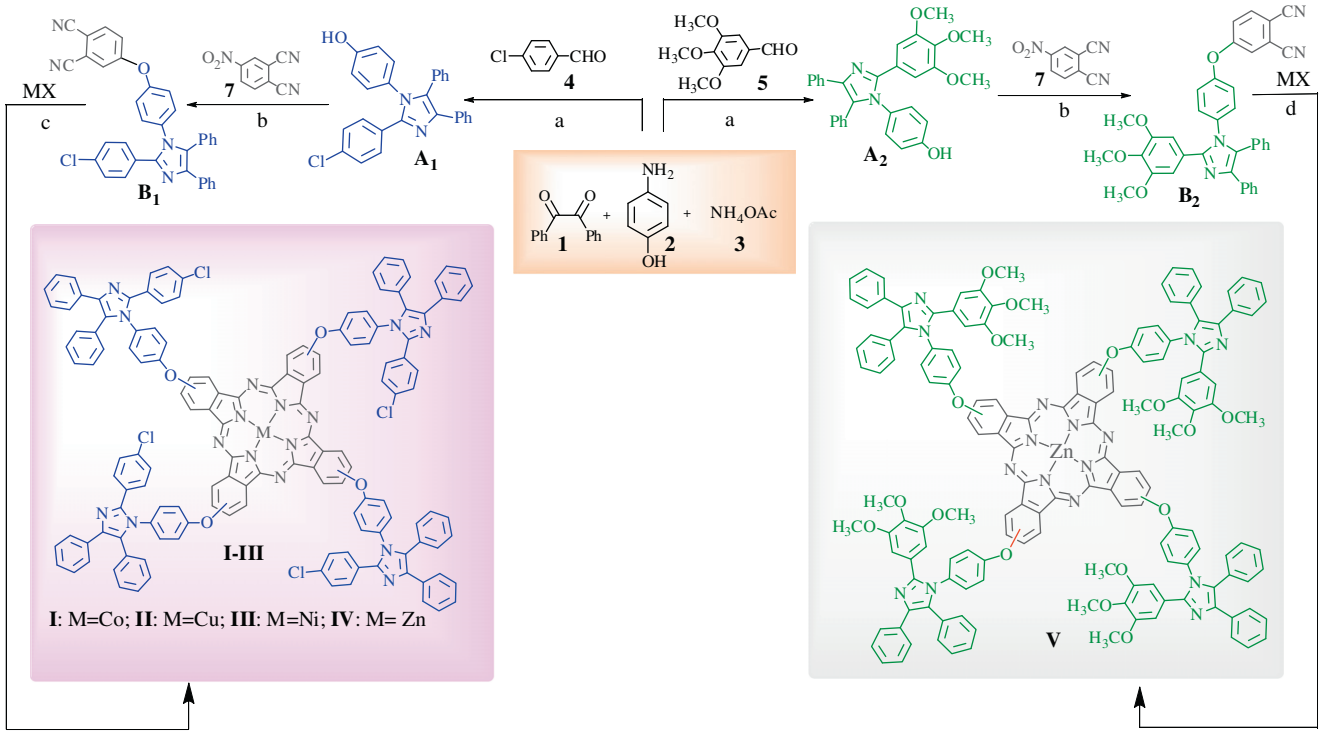
The synthesis of dicyano compounds $\mathbf{B_1}$ and $\mathbf{B_2}$ was carried out by base-catalyzed aromatic nitro displacement of 4-nitrophthalonitrile with $\mathbf{A_1}$ and $\mathbf{A_2}$ in DMF; K_2CO_3 was used as the base for this displacement. The IR spectra of $\mathbf{B_1}$ and $\mathbf{B_2}$ clearly indicated the presence of CN vibrational peaks at 2233, 2227, and 2233 cm^{-1}, respectively. The ^{1}H NMR spectra were also in good agreement with the structures of compounds $\mathbf{B_1}$ and $\mathbf{B_2}$. For instance the spectrum of $\mathbf{B_2}$ exhibited the aliphatic protons as two singlets at δ 3.63 (6H) and 3.67 ppm (3H). The aromatic protons in the low field region appeared as a singlet at δ 6.75 (2H), multiplets at δ 7.18–7.21 (3H), δ 7.25–7.29 (5H), δ 7.34–7.35 (3H), δ 7.42–7.45 (2H), δ 7.50–7.53 (2H), δ 7.55–7.56 (1H), and a doublet at δ 8.17 (1H).

The desired metallophthalocyanines **I–V** were obtained by cyclotetramerization of the dinitriles $\mathbf{B_1}$ and $\mathbf{B_2}$ (3 mmol) in the presence of anhydrous metal salts [$CoCl_2$, CuCl, $NiCl_2$, and $Zn(OAc)_2$] (1 mmol) using DBU as the catalyst in 2-(dimethylamino)ethanol (DMAE) (for $\mathbf{B_1}$) or DMF (for $\mathbf{B_2}$) at reflux temperature. Attempts to obtain CoPc, NiPc, and CuPc from the dinitrile compound $\mathbf{B_2}$ were unsuccessful (Scheme 1).

IR, ^{1}H NMR, MALDI-TOF-MS, and UV–Vis analyses confirmed the proposed structures of the compounds synthesized.

* Corresponding author. Tel.: +98 861 4173400; fax: +98 861 4173406.
E-mail address: a-karimi@araku.ac.ir (A.R. Karimi).

0040-4039/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tetlet.2012.10.071



Scheme 1. Synthesis of metallophthalocyanines **I–V**. Reagents and conditions: (a) WD/SiO_2, 140 °C (A_1): 72%, (A_2): 65%; (b) K_2CO_3, DMF, 24 h, rt, (B_1): 83%, (B_2): 89%; (c) metal salt (MX), DBU, DMAE, N_2, reflux, (**I**): 34%, (**II**): 36%, (**III**): 35%, (**IV**): 41%; (d) $Zn(OAc)_2$, DBU, DMF, N_2, reflux (**V**): 33%.

After conversion of the dinitriles into the metallophthalocyanines, the sharp peak for the CN vibration completely disappeared in the IR spectra. The ^{1}H NMR spectrum of **IV** exhibited aromatic protons as multiplets at δ 7.24–7.32, 7.40–7.45, and 7.51–7.56. In the ^{1}H NMR spectrum of **V**, the aliphatic CH_3 group protons appeared at δ 3.6–3.70 and the aromatic protons were observed as a multiplet at δ 6.74–7.55.

The MALDI-TOF mass spectrum provided evidence for the structure of phthalocyanine **IV** with the presence of the molecular ion peak at 2261.8.

The thermal properties of phthalocyanines **I–V** were analyzed by thermal gravimetric analysis (TGA) in the temperature range of 30–1000 °C under a nitrogen atmosphere with a heating rate of 10 °C/min. The primary weight loss was related to the residual solvent which is typical of a TGA heating run.

The initial decomposition temperatures and the amounts of total mass loss percentages determined from the TG curves are listed in Table 1. The initial decomposition temperatures of the compounds were in the order: **II** > **I** > **V** > **III** > **IV**. No obvious correlation between the transition metal ion in the phthalocyanine and the initial decomposition temperatures was evident.

Phthalocyanines **I**, **IV**, and **V** displayed good solubility in DMSO, DMF, chloroform, and THF. Phthalocyanine **II** was soluble in THF but only slightly in DMF. Phthalocyanine III was soluble in THF and DMF.

Table 1
Thermal analyses data for **I–V**

Pc	Initial dec temp (°C)	Mass loss up to 1000 °C (%)
I	320	65.80
II	340	69.33
III	280	93.97
IV	246	58.92
V	300	80.95

The UV/Vis spectra of the metal Pc complexes consisted of two strong absorption regions at 600–700 nm (Q band) and around 300–400 nm (B band). The UV/Vis spectra of phthalocyanines **I–V** in THF are shown in Figure 1 and demonstrated single intense bands at 658, 671, 668, 677, and 669 nm, respectively. There was also a shoulder at a slightly higher energy for all the phthalocyanines. Weaker absorptions appeared at 597, 604, 602, 606, and 606 nm for phthalocyanines **I–V**, respectively. This is typical of metal complexes of substituted and unsubstituted metallophthalocyanines with D_4h symmetry.[22] The B bands for **I–V** were observed at 298; 296, 253; 298, 253; 346, 296; 349, 296 nm, respectively (Fig. 1 and Table 2).

Aggregation is usually a coplanar association and is dependent on the nature of the solvent, the concentration, the metal ion, the nature of substituents, and the temperature.[23] In this study the aggregation behavior of these complexes was investigated at different concentrations in various solvents. The aggregation behavior of phthalocyanines **I**, **IV**, and **V** at five concentrations (5×10^{-5}, 4×10^{-5}, 3×10^{-5}, 2×10^{-5}, and 1×10^{-5} M) in DMSO, DMF,

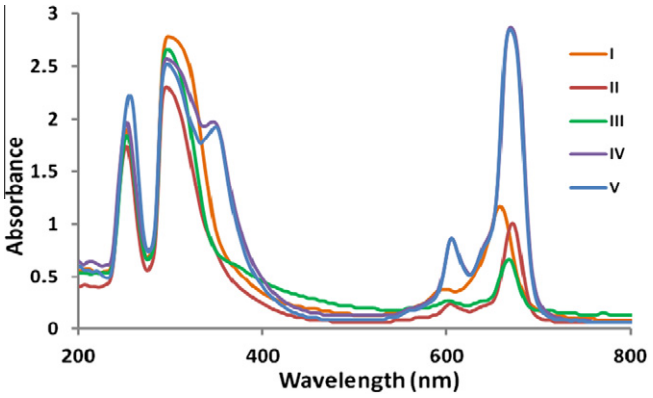


Figure 1. UV/Vis absorption spectra of **I–V** in THF ($c = 3 \times 10^{-5}$ M).

Table 2
Absorption data for phthalocyanines **I–V** in THF ($c = 3 \times 10^{-5}$ M)

Pc	λ_{max} (nm) (log ε)
I	658 (4.59), 597 (4.10), 298 (4.97)
II	671 (4.53), 604 (3.90), 296 (4.89), 253 (4.76)
III	668 (4.34), 602 (3.95), 298 (4.95), 253 (4.79)
IV	677 (4.22), 606 (3.75), 346 (4.24), 296 (4.73)
V	669 (4.98), 606 (4.46), 349 (4.8), 296 (4.93)

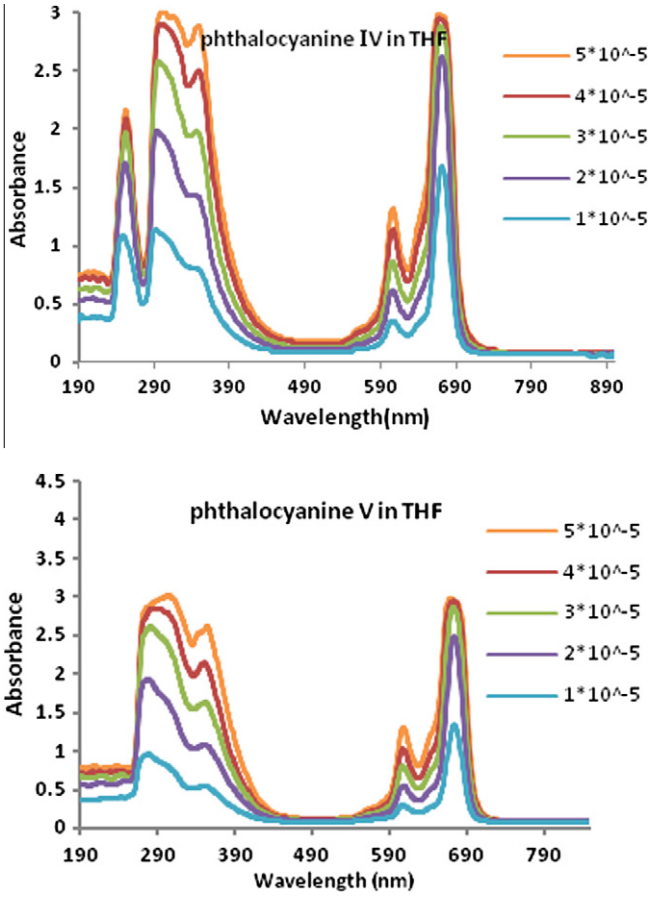


Figure 2. UV/Vis absorption spectra of **IV** and **V** in THF at different concentrations.

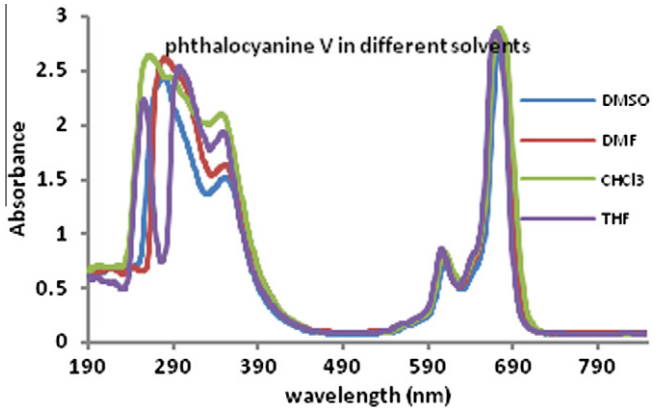


Figure 3. UV/Vis absorption spectra of **V** in different solvents ($c = 3 \times 10^{-5}$ M).

chloroform, and THF were studied. The intensity of the absorption bands at 600–700 nm increased on increasing the concentration

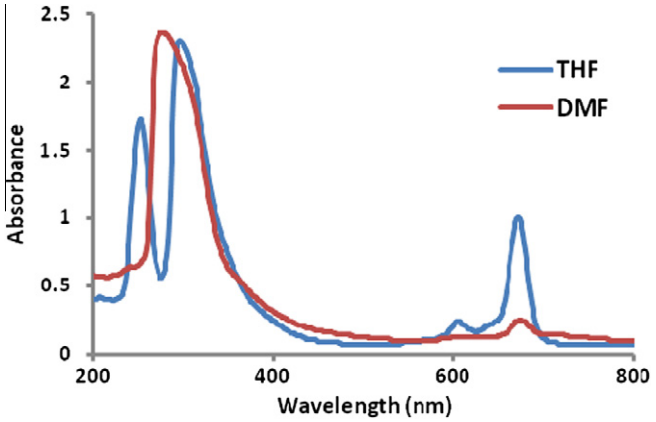


Figure 4. UV/Vis absorption spectra of **II** in THF and DMF ($c = 3 \times 10^{-5}$ M).

and there were no new bands due to aggregated species. Hence, phthalocyanines **I**, **IV**, and **V** did not show aggregation in these solvents (Figs. 2 and 3).

In addition, the aggregation behavior of phthalocyanines **II** and **III** was investigated in DMF and THF at different concentrations, as above. While phthalocyanine **II** did not show aggregation in THF, it showed aggregation in DMF as was apparent by the decrease in the absorbance intensity[24] (Fig. 4).

Phthalocyanine **III** did not show aggregation in THF or DMF. It is noteworthy that among the phthalocyanines synthesized in this study, phthalocyanine **V** has the highest molar extinction coefficient in the visible region in all the considered solvents.

In conclusion, we have synthesized and characterized five new mononuclear phthalocyanines **I–V**. Phthalocyanines **I**, **IV**, and **V** had the best solubility and did not show aggregation in DMSO, DMF, THF, or $CHCl_3$. Phthalocyanine **II** did not show aggregation in THF, but did aggregate in DMF. Phthalocyanine **III** displayed monomeric behavior in THF and DMF. Phthalocyanine **V** had the highest molar extinction coefficient in the visible region and thus may show better results in PDT.

Acknowledgments

We gratefully acknowledge the financial support from the Research Council of Arak University.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.10.071.

References and notes

1. Zhang, W.; Ishimaru, A.; Onouchi, H.; Rai, R.; Saxena, A.; Ohira, A.; Ishikawa, M.; Naito, M.; Fujiki, M. *J. New Chem.* **2010**, *34*, 2310.
2. Herlambang, S.; Kumagai, M.; Nomoto, T.; Horie, S.; Fukushima, S.; Oba, M.; Miyazaki, K.; Morimoto, Y.; Nishiyama, N.; Kataoka, K. *J. Control. Release* **2011**, *155*, 449.
3. Sizun, T.; Bouvet, M.; Chen, Y.; Suisse, J.; Barochi, G.; Rossignol, J. *Sensor. Actuat. B-Chem.* **2011**, *159*, 163.
4. (a) Lee, W.; Yuk, S. B.; Choi, J.; Jung, D. H.; Choi, S. H.; Park, J.; Kim, J. P. *Dyes Pigments* **2012**, *92*, 942; (b) Yuksel, F.; Durmuş, M.; Ahsen, V. *Dyes Pigments* **2011**, *90*, 191.
5. Leznoff, C. C.; Lever, A. B. P. In *Phthalocyanines, Properties and Applications*; VCH: New York, 1996; Vol. 4,
6. Li, D.; Le, Y.; Hou, X. Y.; Chen, J. F.; Shen, Z. G. *Synth. Met.* **2011**, *161*, 1270.
7. Zhang, Y.; Cai, X.; Bian, Y.; Jiang, J. *Struct. Bond.* **2010**, *135*, 275.
8. (a) Vacus, J.; Simon, J. *Adv. Mater.* **1995**, *7*, 797; (b) Kameyama, K.; Satake, A.; Kobuke, Y. *Tetrahedron Lett.* **2004**, *45*, 7617; (c) Ogunsipe, A.; Nyokong, T.; Durmus, M. *J. Porphyrins Phthalocyanines* **2007**, *11*, 635; (d) Idowu, M.; Nyokong, T. J. *Luminescence* **2009**, *129*, 356.

9. Sharon, N.; Lis, H. *Science* **1989**, *246*, 227.
10. Ramezani, M. K.; Oliver, D. P.; Kookana, R. S.; Lao, W.; Gill, G.; Preston, C. *Chemosphere* **2010**, *79*, 1040.
11. Gaonkar, S. L.; Lokanatha Rai, K. M.; Suchetha Shetty, N. *Med. Chem. Res.* **2009**, *18*, 221.
12. Antolini, M.; Bozzoli, A.; Ghiron, C.; Kennedy, G.; Rossi, T.; Ursini, A. *Bioorg. Med. Chem. Lett.* **1999**, *9*, 1023.
13. Wang, L.; Woods, K. W.; Li, Q.; Barr, K. J.; McCroskey, R. W.; Hannick, S. M.; Gherke, L.; Credo, R. B.; Hui, Y.-H.; Marsh, K.; Warner, R.; Lee, J. Y.; Zielinsky-Mozng, N.; Frost, D.; Rosenberg, S. H.; Sham, H. L. *J. Med. Chem.* **2002**, *45*, 1697.
14. Sham, M. S.; Shubhi, J.; Monica, D.; Ashok, K. *Med. Chem.* **2008**, *4*, 146.
15. Lee, J. C.; Laydon, J. T.; McDonnell, P. C.; Gallagher, T. F.; Kumar, S.; Green, D.; McNully, D.; Blumenthal, M.; Heys, J. R.; Landvatter, S. W.; Strickler, J. E.; McLaughlin, M. M.; Siemens, I. R.; Fisher, S. M.; Livi, J. P.; White, J. R.; Adams, J. L.; Young, P. R. *Nature* **1994**, *372*, 739.
16. Satoru, I. Japn Kokkai Tokyo Koho JP 01, 117, 867, 1989; *Chem. Abstr.* 1989, *111*, 214482.
17. Bossche, H. V. D.; Willemsens, G.; Cools, W.; Marichal, P.; Lauwers, W. *Biochem. Soc. Trans.* **1983**, *11*, 665.
18. Freedman, J.; Loscalzo, J. *New Therapeutic Agents in Thrombosis and Thrombolysis*, 3rd ed.; Taylor and Francis, 2009.
19. El-Khouly, M. E.; Rogers, L. M.; Zandler, M. E.; Suresh, G.; Fujitsuka, M.; Ito, O.; Souza, F. D. *ChemPhysChem* **2003**, *4*, 474.
20. (a) Karimi, A. R.; Alimohammadi, Z.; Amini, M. M. *Mol. Divers.* **2010**, *14*, 635; (b) Karimi, A. R.; Alimohammadi, Z.; Azizian, J.; Mohammadi, A. A.; Mohmmadizadeh, M. R. *Catal. Commun.* **2006**, *7*, 728.
21. (a) Karimi, A. R.; Bayat, F. *Tetrahedron Lett.* **2012**, *53*, 123; (b) Karimi, A. R.; Khodadadi, A. *Tetrahedron Lett.* **2012**, *53*, 5223.
22. Riesen, A.; Zehnder, M.; Kaden, T. A. *Helv. Chim. Acta* **1986**, *69*, 2074.
23. Enkelkamp, H.; Nolte, R. J. M. *J. Porphyrins Phthalocyanines* **2000**, *4*, 454.
24. Pawlowski, G.; Hanack, M. *Synthesis* **1980**, 287.