

History, development, and a new concept of phthalocyanines in Turkey

Özer BEKAROĞLU*

Department of Chemistry, İstanbul Technical University, Maslak, İstanbul, Turkey

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Abstract: This paper reviews the history of phthalocyanines in Turkey. Phthalocyanines are chemical compounds that were accidentally discovered nearly a century ago. The relevant research and articles have grown dramatically in Turkey since our first paper on them containing four [15]crown[5] published in 1986. The ball-type phthalocyanines were produced and published as a new concept in phthalocyanine chemistry for the first time by our group in Turkey in 2006. Unfortunately, with the exception of our work on this subject, almost no papers have been published in Turkey or in other countries since then. We strongly urge scientists to consider working on this new type of phthalocyanine, which shows interesting development potential in electrical, electrochemical, and photovoltaic applications as well as oxygen reduction for fuel cells.

Key words: Turkey, phthalocyanines, history, development, new concept

1. Introduction

Metal-free phthalocyanine (H_2Pc) was obtained by accident for the first time in 1907 as a by-product during the preparation of 2-cyanobenzamide.¹ Twenty years after this discovery, copper phthalocyanine was synthesized by Disbach and his coworker from 1,2-dibromobenzene in 1927. Linstead and his coworkers prepared several metallophthalocyanines (MPc) by developing synthetic methods and elucidated the structure of phthalocyanines (Pcs). X-ray diffraction analyses of them were performed by Robertson.¹

The name phthalocyanine was first used by Linstead. Pcs are synthetic macrocycles structurally similar to naturally available porphyrins such as hemoglobin, chlorophyll, and vitamin B₁₂. They can be regarded as tetrabenzotetraazaporphyrins and as tetramereization products of 4 iso-indoline units and consist of a planar structure with an 18 π -electron system. They are very stable blue or green pigments and dyes, an important class of chemicals for commercial use in many areas of technology.¹

As a blue pigment CuPc was first produced industrially in 1935 by an English company and then other companies in Germany and the USA. Today, CuPc and peripherally or nonperipherally substituted derivatives, and about 70 different elements including metals and some metalloids have been used as central atoms in all kinds of Pcs.

The first Pc containing four [15-crown-5] was given to a coworker who had just finished his PhD under my supervision and wanted to work with me further in 1982. Unfortunately, he could not synthesize the compound at that time, because he believed that such compounds could not be prepared. Apparently, he decided not to work on these Pcs, as we learned later. During my work at the state-owned Scientific and Technological Research Council of Turkey (TÜBİTAK) at Gebze, İstanbul, as Department Head of the Chemistry and Instrumental

*Correspondence: obek@itu.edu.tr

Analyses Laboratories, another of my former PhD students completed the synthesis of copper phthalocyanine containing [15-crown-5] in which crown ether units are integral parts of the molecule in 1985 (Figure 1).² A similar compound was also reported independently by another 2 groups in the same journal in the subsequent 2 months.^{3,4}

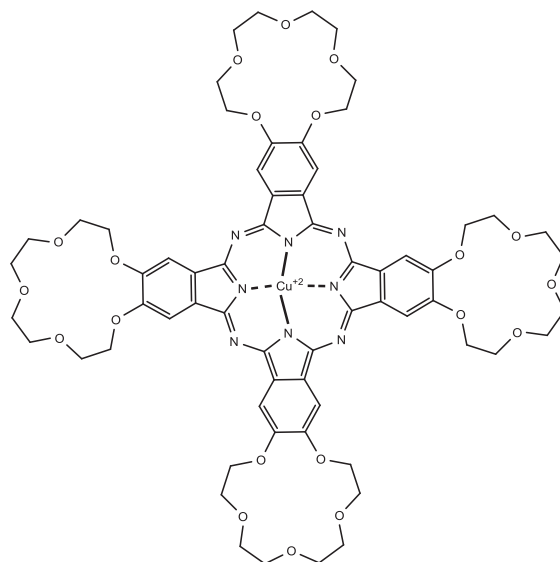


Figure 1. Pc containing four [15]crown[5].²

These compounds have received great attention from the scientific community. Their mesophase and electrochemical properties, in particular, have been measured by a joint research and the results have been published.^{5,6}

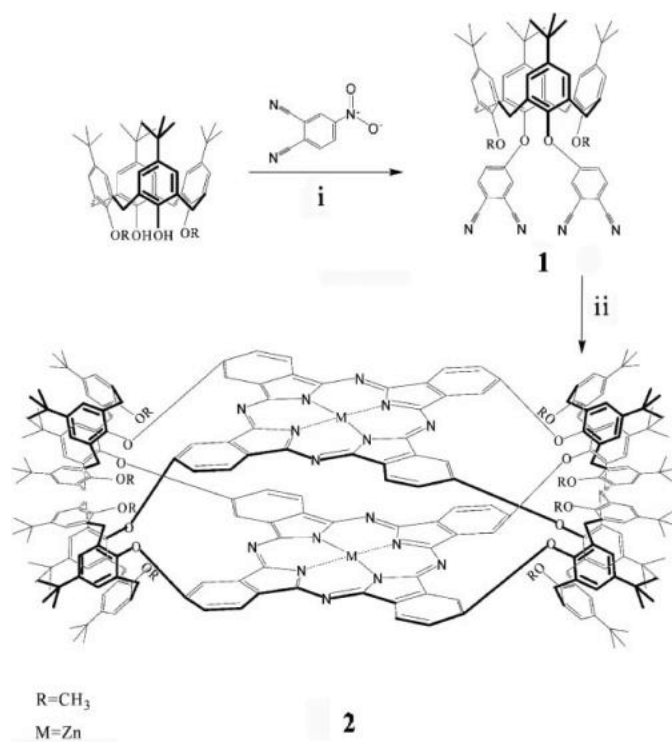
We have persevered to design and synthesize novel Pcs substituted with different crown ether, azacrown ether, alkylthia ether, 2-fold-macrocyclic, unsymmetrical, network-polymer and with different homo and hetero metal ions. We have measured electrical and electrochemical properties with my PhD students, coworkers, and numerous researchers abroad.^{7–55} In the meantime, my former PhD and postdoctoral students and their PhD students have started working on Pcs. In a short time, the number of scientists working on this subject along with their publications has grown considerably in many universities. Since my retirement in 2000, I have continued to work on Pcs upon invitations from several universities. The characteristic properties of Pcs, such as intense colors, high intrinsic conductivity, redox activity, very high thermal stability, and other special properties, make Pcs and metallo Pcs suitable for many applications. In particular, lanthanide and lutetium series metallo Pcs attract attention in the field of molecular electronics such as for optical displays, photovoltaic cells, and organic light emitting diodes. Electrical direct current (dc) and alternating current (ac) measurements of Pc films are decisive to study the relevant conduction mechanism for their films' applications. Our interest has been focused on the synthesis of double decker novel lutetium Pc. Revisiting a previously published dimeric Pc³⁸ dilutetium tetraphthalocyanine has been synthesized and the charge transport mechanism investigated.^{56–59}

2. Ball-type phthalocyanines

Ball-type or face-to-face diphthalocyanines were thought of as a new concept around 2000. One already published compound⁶⁰ was found to be appropriate to prepare a ball-type Pc, but all attempts to make that compound

a ball-type Pc failed. In the meantime, a group in Russia published the first ball-type ZnPc containing *o*-phenylidene bridges by the reaction of [1,2-bis(3,4-dicyanophenoxymethyl)-benzene] with zinc acetate and 1,8-diaza bicyclo[5.4.0]undec-7-ene (DBU) as base in boiling dichlorobenzene under argon atmosphere for 14 h. The yield of this compound was rather low, 1.84%.⁶¹ In the next study by this group, the same ball-type Pc was prepared by the solid-phase increasing zinc acetate by a factor of 10 and heating the reaction mixture in the absence of catalysts in microwave oven at 250 °C for 5 min this time; the yield of reaction was 33%.⁶²

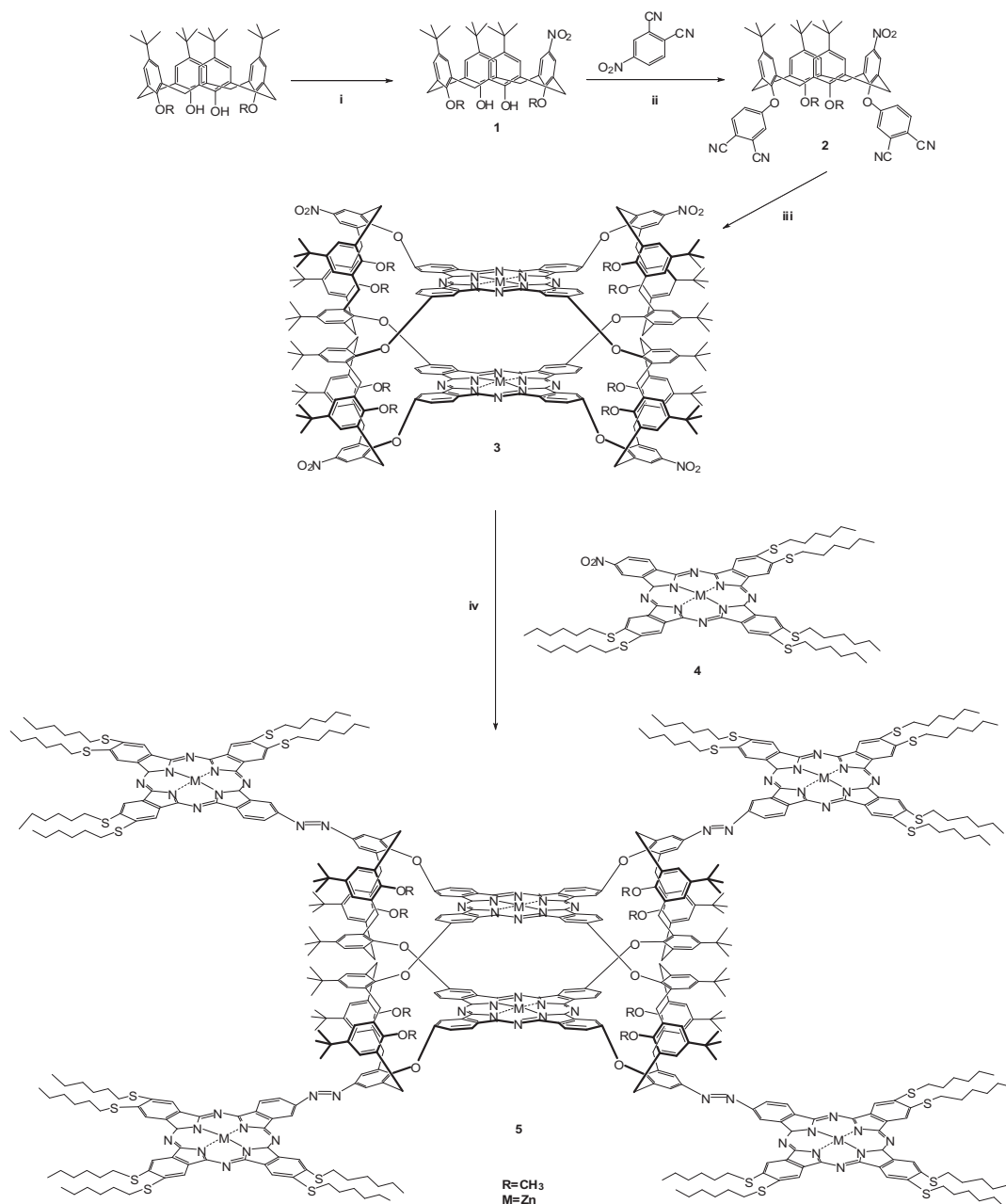
The first ball-type metal-free and metallo Zn₂Pc₂ containing 4 [calix[4]arene] units as bridges was published by our group in 2006 (Scheme 1).⁶³ The compound was obtained by the mixture of phthalonitrile of [calix[4]arene] and zinc acetate with refluxing for 23 h in dry dimethyl formamide (DMF) under nitrogen atmosphere. The yield was 6.5%.



Scheme 1. The synthesis of [calix[4]arene] bridged ball-type zinc Pc.⁶³

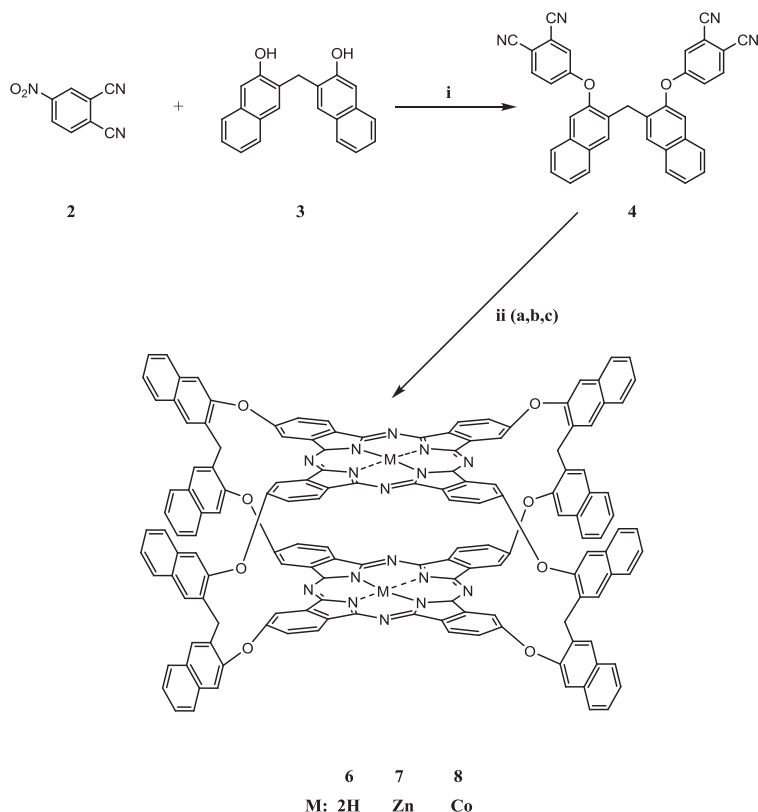
The cyclic voltammetric (CV) and electrical measurements of both metallo and metal-free ball-type Pc have been carried out on platinum in dimethyl sulfoxide (DMSO) and in spin-coated film, respectively. The CV studies of ball-type H₄Pc₂ and Zn₂Pc₂ have shown ring centered type mixed-valence behavior as a result of the strong interaction between the 2 Pc rings, and the comproportionation constants for both compounds indicate that those mixed-valence species are highly stable. Dc and detailed impedance spectroscopy techniques have been used to investigate the charge transport mechanism and gas sensing properties of spin coated film of Zn₂Pc₂ as a function of temperature and gas concentration. A strong deviation from the Arrhenius law was observed for this film as in fast ion conducting glasses, which are the fundamental of electrochemical energy-based devices. The measured ac conductivity data were explained by the correlated barrier hopping model. The response characteristics of the film for the toluene vapor were also investigated. Very high sensitivity was obtained for the 50 ppm toluene vapor at room temperature.^{63,64}

Starting from [5,11,17,23-tetra-tert-butyl-25,27-dihydroxy-26,28-dimethoxycalix[4]arene-mononitro], ball-type with 4 hexyl-thio-hexametallo-phthalocyanines were synthesized, and their electrical and spectroelectrochemical properties were investigated.⁶⁵ Later, the third order nonlinear optical properties of those ball-type Zn_2Pc_2 with 4 calix[4]arene (Scheme 2) in chloroform solution were measured by Z-scan technique with a nanosecond laser at 532 nm wavelength pulses.^{59,66}



Scheme 2. The synthesis of ball-type hexanuclear metallophthalocyanine, bridged by calix[4]arenes substituted with 4 hexylthiometallophthalocyanines. Synthetic pathway for compounds **1–3** and **5** [(i) HNO_3 , CH_2Cl_2 , CH_3COOH ; (ii) K_2CO_3 , DMSO, 70 h, 80 °C; (iii) $Zn(OAc)_2 \cdot 2H_2O$, DBU, 1-pentanol, reflux; (iv) NaOH solution, powdered Zn , MeOH/THF, reflux, 18 h].⁶⁵

A suspension of [4,4'-[1,1'-methylenebis(naphtalene-2,1-diyl)]bis(oxy)dinaphthalonitrile] (MOD) in dry amyl alcohol and lithium metal in sealed tube was heated at 170 °C for 8 h metal-free ball-type H_4Pc_2 was obtained with a yield of 10% (Scheme 3).^{59,67} If this starting compound MOD was mixed with the zinc acetate and heated in a sealed tube without solvent at 280 °C for 3 min, ball-type Zn_2Pc_2 was obtained. If cobalt acetate was used instead of zinc at the same temperature in 5 min ball-type Co_2Pc_2 was obtained. The yields were 9.75% and 7.75% respectively. The electrical and spectroelectrochemical properties of metal-free, Zn and Co ball-type Pcs have been measured. From impedance spectra the bulk resistance was observed, which showed a typical negative temperature coefficient of resistance, decreasing with a rise in temperature, like those of a semiconductor.



Scheme 3. The synthesis of ball-type Pc bridged 4 MOD.^{59,67}

Furthermore, the reaction of MOD with the cobalt salt in a solid phase at 320 °C for 10 min and washing the reaction mixture with hot methanol and acetic acid gave a mixture of several Pcs. MALDI-TOF mass measurements of those mixture with the matrix of 2,5-dihydroxybenzoic acid showed that not only ball-type Co_2Pc_2 but also 4 more novel CoPcs in different structures were produced (Figures 2 and 3).⁵⁹

[1a,8b-Dihydronaphtho[b]naphthofuro-[3,2.d]furan-7,10-diyl] was converted to nitrile derivative then was heated with zinc or cobalt salts in a sealed tube at 300 °C for 5 min without solvent resulting in 2 type of Pcs: one was mono zinc or cobalt Pc and the other was ball-type zinc or cobalt Pc with yields of 5% and 4.5% for mono and 15% and 14% for ball-type Pcs, respectively. When dinitrile derivative was heated with lithium metal in hexanol at 170 °C for 8 h, only metal free mono across adjacent ring formed Pc was obtained. However, when the same nitrile was heated with magnesium acetate without solvent in a sealed tube at 300 °C for 5 min both metal free mono and metal free ball-type Pcs were formed.⁵⁹

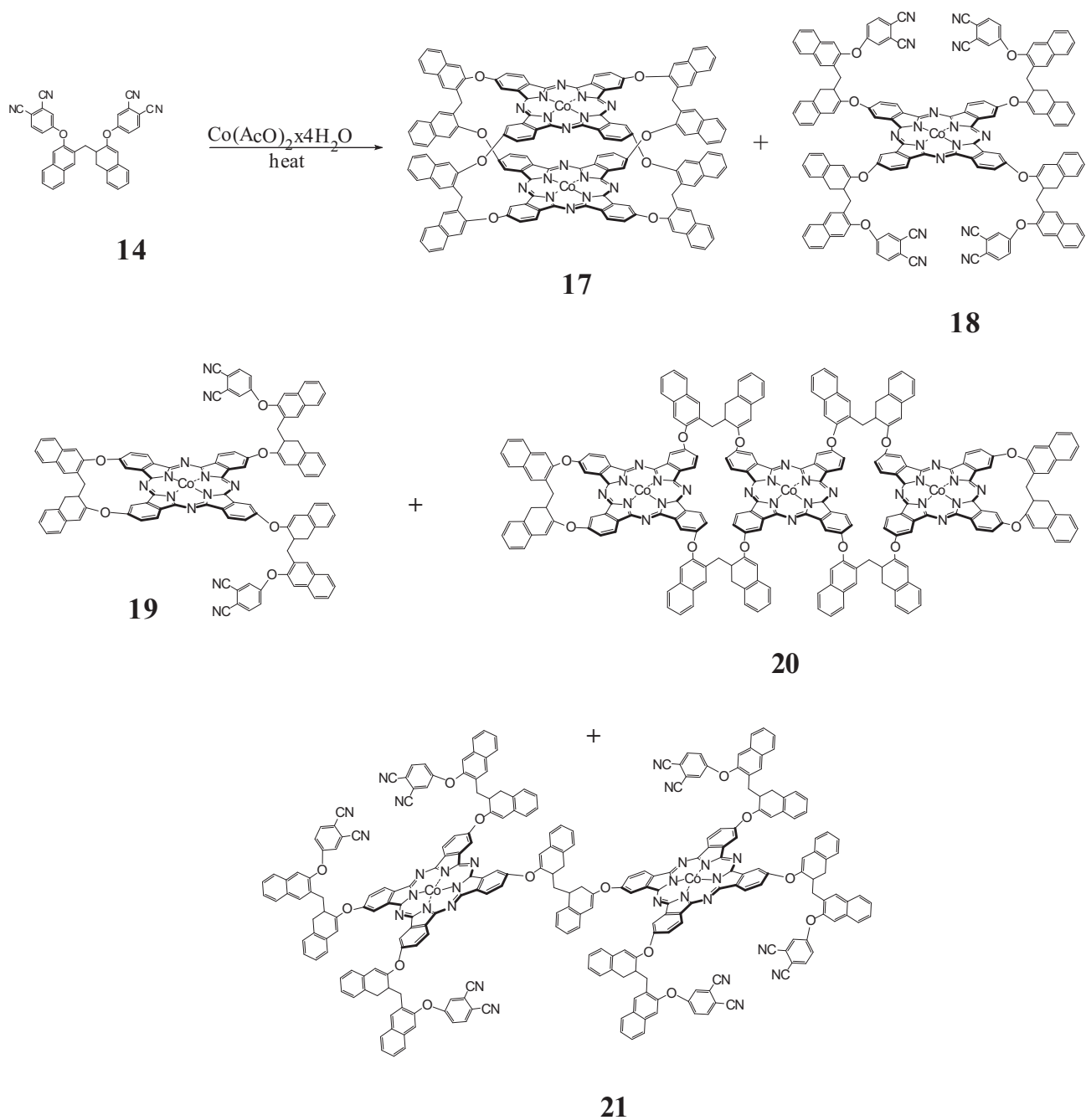


Figure 2. Different Pcs produced in the mixture of the reaction of MOD with cobalt salt.⁵⁹

Pentaerythritol with 4 hydroxy groups has also been used for preparation of ball-type Pcs. To obtain the starting bisphthalonitrile 2 of the 4 hydroxy groups of pentaerythritol were protected with benzaldehyde first as mono acetal. Heating a mixture of those benzaldehyde mono acetal and metal salts in a sealed tube at 300 °C for 10 min the zinc or cobalt ball-type Pcs formed with yields of 23% and 18%, respectively. After removing the mono acetal groups by hydrogenation, ball-type Pcs with 8 free hydroxy groups or water-soluble alkali metal salts of ball-type Pcs were obtained.⁵⁹

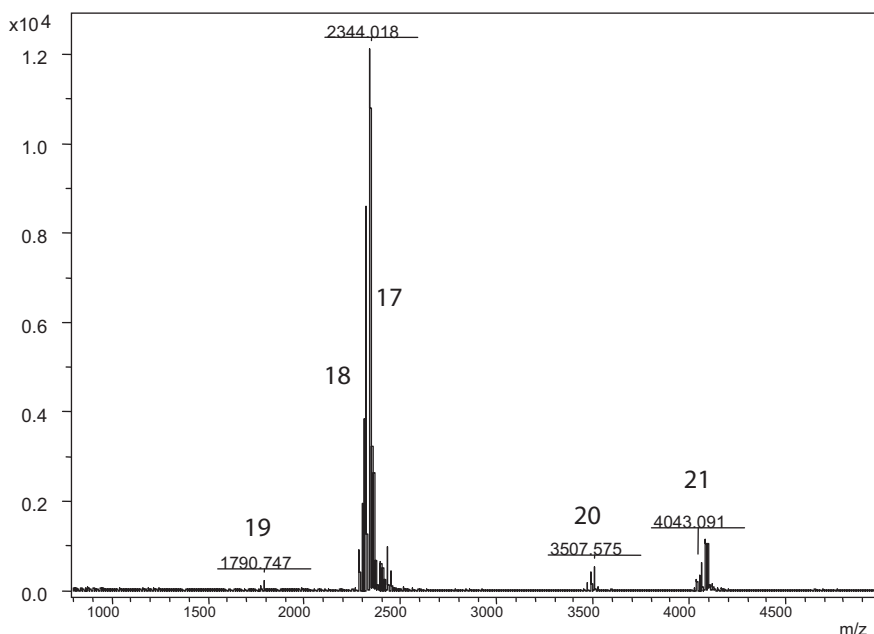
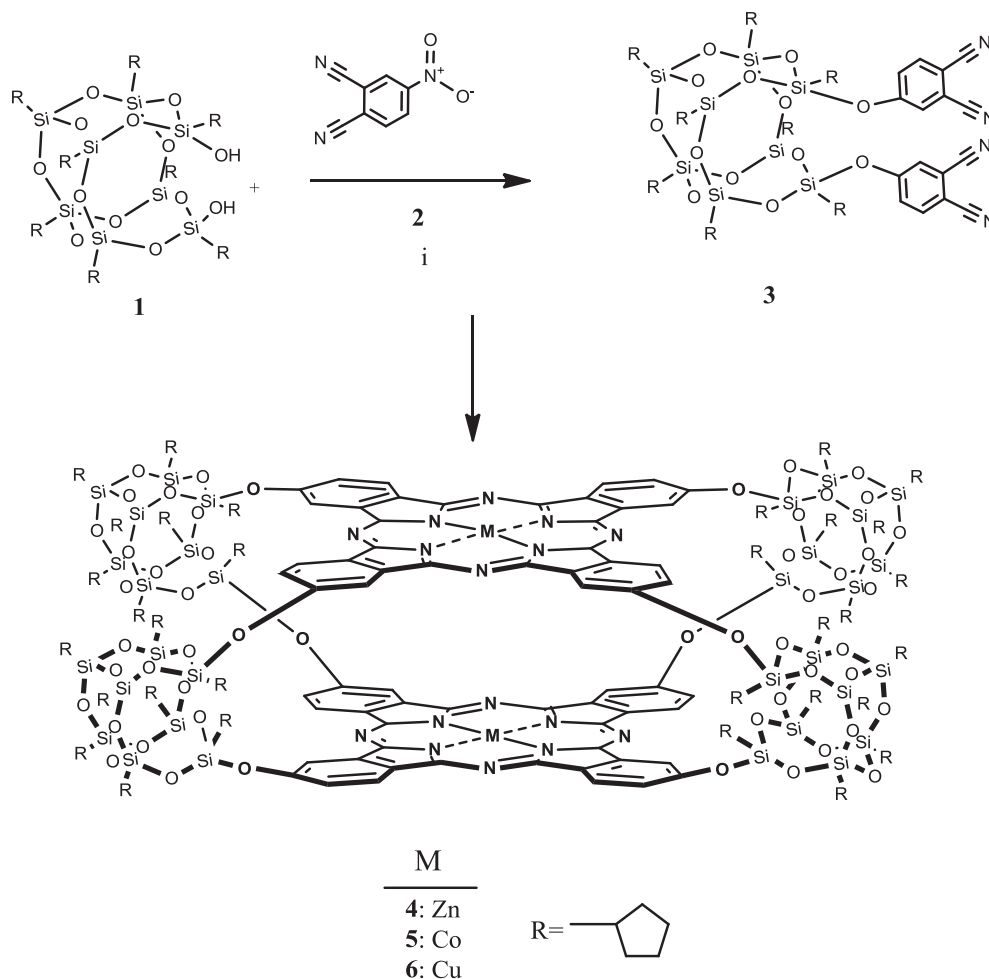


Figure 3. The MALDI-TOF spectra of mixture of compounds given in Figure 2.⁵⁹

Those free 8 hydroxy groups of the ball-type Pcs give the possibility to make further reactions to obtain novel ball-type Pcs with various properties. For example, the 8 hydroxy groups can be converted to 4 crown ethers or to 8 perfluorodecyl units.⁵⁹ Those Pcs have been shown to be one of the most promising optical limiting (OL) materials for nanosecond 532 nm laser pulses. OL refers to a decrease in the optical transmittance of a material with increasing incident light intensity, which is considered a powerful means of protection for laser applications. Pcs have a relatively low linear absorption and a high ratio of excited-state to ground-state absorption cross sections in the range 400–600 nm.⁶⁸ Pcs exhibit reverse saturated absorption (RSA), which can limit the output energy of incident light effectively as they are used in optical limiters. The excellent properties of Mpc as candidates for OL applications originate not only from their extensive π -electron delocalization and their thermal and chemical stability, but also from their processability by either substituting the peripheral or axial side groups or changing the central metal ion.⁶⁹ Recently, we investigated nonlinear absorption of octakis(mercaptopropylisobutyl-POSS) substituted MPcs (Co, Cu, Zn).⁷⁰ Among them, CuPc has a very good nonlinear absorption and a very good combination of the OL parameters. These results encouraged us to prepare sandwich complexes of LuPc₂ and GdPc₂ that contain [octakis (mercaptopropylisobutyl-POSS)] functional group on each Pc moiety. After the OL studies, both compounds showed nonlinear absorption, and excellent combinations of the optical limiting parameters for LuPc₂ make it a very good candidate as an OL material. The electrochemical study of the cast film of LuPc₂ indicated that this compound can be used as a component in electrochromic devices for the green–blue transition.⁶⁸

In the meantime, we synthesized ball-type M₂Pc₂ of (Zn, Co, Cu) containing 4 [cyclopentylsilanoxy-POSS] bridged groups (Scheme 3), and electrocatalytic properties of these M₂Pc₂'s toward the oxygen reduction reaction (ORR) were investigated by the rotating disk electrode (RDE) technique. The limiting current for the first wave implies that ORR probably occurs via peroxo species, producing water as the main product and some hydrogen peroxide as the side product. The second wave appears at considerably negative potentials that possibly correspond to the reduction of hydrogen peroxide to water. The nature of this wave was discussed

by the rotating ring-disk electrode (RRDE) technique. The comparison of the electrocatalytic performances of mono nuclear CoPc and ball-type Co_2Pc_2 with similar substituents shows that the macrocyclic structure has a remarkable influence on the kinetics of ORR. The higher performance of ball-type Co_2Pc_2 should be related to the presence of 2 redox-active face-to-face metal centers. This promotes the interaction with oxygen molecules, likely the O–O bond breakage and thus reduction to water.⁷¹ Detailed comparison and interpretation of the results included the activity of a platinum-based catalyst, which is the best at the present time due to its high catalytic activity and long-time stability in the full cell field although it is very expensive.



Scheme 4. The synthesis of ball-type Pcs containing 4 [cyclopentyl-disilanoxy-POSS] bridges.⁷¹

Regarding RDE measurements, the catalytic activity of the ball-type Co_2Pc_2 (Scheme 4) was observed to be superior when compared to those of ball-type Zn and Cu Pc and mono Pc of the same starting material, implying that the presence of 2 co-facial redox-active cobalt centers in the ball-type structure promotes the interaction with oxygen molecules and the tendency for the formation of μ -peroxo species and thus reduction to water. The investigation also showed that the bridging compounds have a remarkable effect on the catalytic performances of ball-type Pcs. The ball-type Co_2Pc_2 based catalyst in this work displays the best water selectivity and oxygen reduction activity among all Pc-based catalysts tested in our electrochemistry laboratory to date. In addition to the excellent catalytic activity of this compound, the variation of oxygen reduction

current density with time suggested that its stability is much higher than that of the platinum based one under our experimental conditions.

The ball-type Zn, Co, Cu Pcs were prepared starting with [1,4-bis(dicyanothio)erythritol]. After characterization of the compounds, their electrochemical, electrocatalytic, electrical, and gas sensing properties were investigated (Figure 4).⁷²

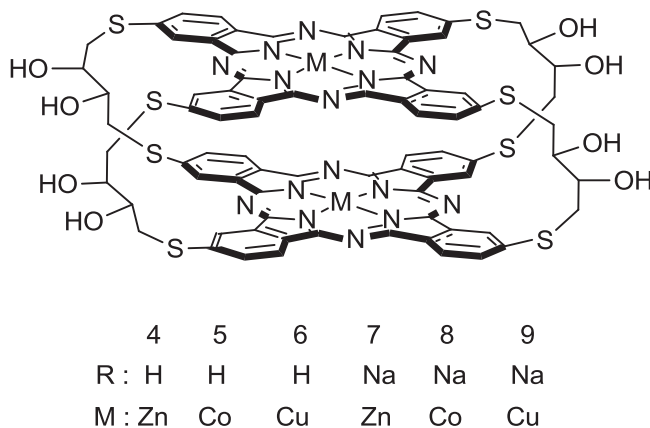


Figure 4. The structure of ball-type (Zn, Co, Cu) Pc bridged of [1,4-bis(dicyanothio)erythritol].⁷²

The voltammetric studies of the ball-type complexes Zn_2Pc_2 and Cu_2Pc_2 showed ring-centered type mixed-valence behavior as a result of electronic coupling between the 2 MPc units. However, the intramolecular interaction appears to be very weak, because of low potential differences between the peaks observed as a result of splitting. In this study, only Co_2Pc_2 showed remarkable catalytic activity towards ORR in acidic medium.

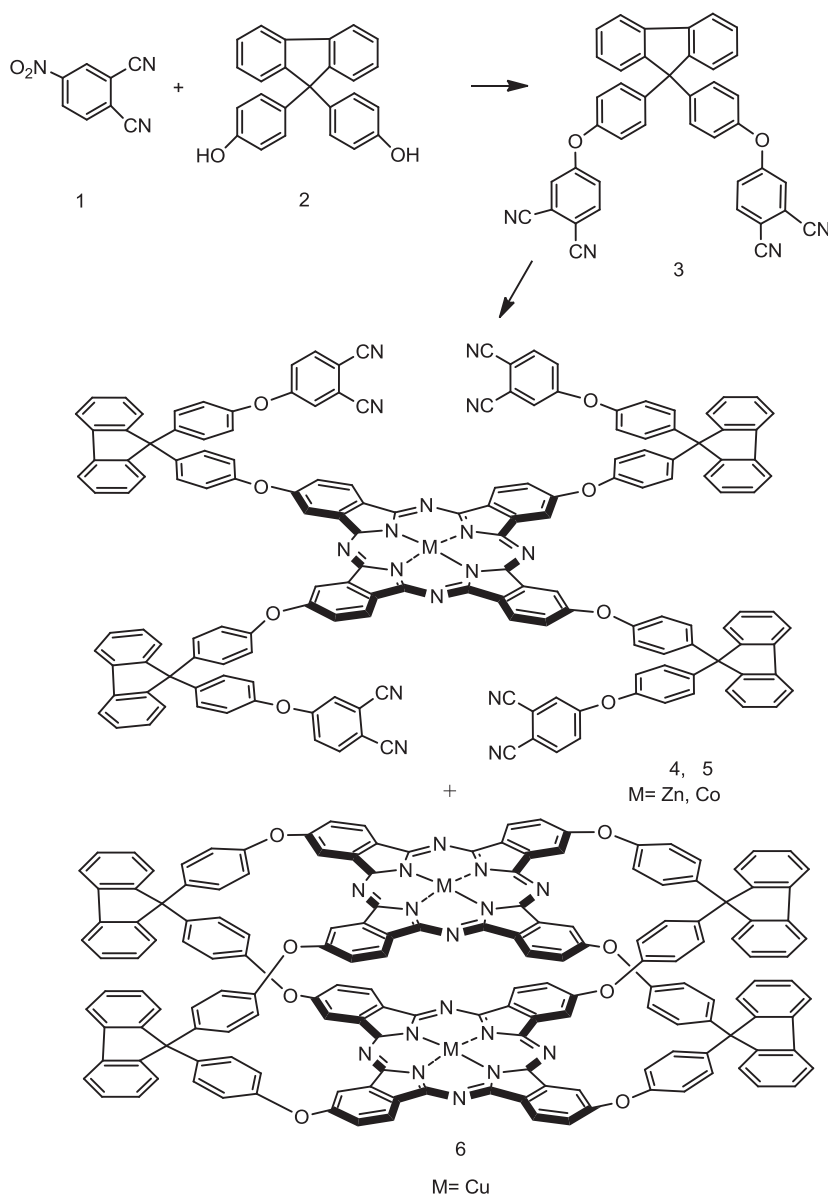
Spin-coated films were investigated for application as carbon dioxide gas sensors. All 3 compounds were found to be highly sensitive to carbon dioxide and their response and recovery characteristics depend on the gas concentration. The Cu_2Pc_2 -coated sensor can detect as low as 100 ppm of carbon dioxide gas.

According to our observations, the electrical, electrochemical, and other properties of the ball-type Pcs depend strongly on the structure of the bridged compounds between face-to-face Pc units. Therefore, we have tried several types of compounds like electron acceptors or electron donors, and aliphatic or aromatic and heterocyclic compounds to prepare ball-type metal-free and metallo Pcs. One of them was [9,9-bis(4-hydroxyphenyl)fluorene]. After preparation of our key starting compound dibenzonitrile, we tried to synthesize ball-type Zn, Co, and Cu Pcs. In the same reaction conditions only copper gave ball-type Pc; zinc and cobalt formed mono Pcs (Scheme 5).⁷³ Copper metal probably has a strong template effect and forms very strong and high symmetry Pc.

The electrochemical properties of all complexes studied by cyclic and square wave voltammetry showed that all the complexes have 2 oxidation and 3 reduction potentials. Oxidation and reduction potentials of zinc and cobalt Pcs were found to be lower than those of ball-type copper Pc. This makes the copper Pc more stable against oxidation and reduction; therefore higher potential is required to oxidize and reduce the copper Pc. This could be attributed to the ball-type structure of the copper Pc.

The effect of temperature ac and dc conductivity showed that the ac conductivity varies with frequency, suggesting a hopping conduction mechanism for all compounds. The SO_2 sensing experiment of the film of Co_2Pc_2 exhibited very good SO_2 sensing properties, fast response and recovery rate, repeatability, and high sensitivity that is higher than that of any of the previously reported Pc based gas sensors at the same

SO₂ concentration. This result indicates that the sensor has a very stable and reproducible SO₂ sensing characteristic.



Scheme 5. The synthesis of mono and ball-type Pcs of [9,9-bis(4-hydroxyphenyl)fluorene].⁷³

The nature of metal centers also leads to considerable changes in the properties of ball-type Pc. Therefore, our continuing efforts in the design of novel bridged compounds with applicability in various technological areas encouraged us to synthesize novel ball-type Pcs with different metals. Dicumarol was one of our choices as bridged units to work for new ball-type Pcs. Zn and Co ball-type Pcs were synthesized by heating of the solid phase under nitrogen at 300 °C for 5 min. (Figures 5–7).⁷⁴ A set of organic photovoltaic cells based on Co₂Pc₂ and Zn₂Pc₂ donor molecules and C₆₀ acceptor molecules was prepared. Investigation of the effects of active layer thickness on the performance of the photovoltaic cells indicates that the performance parameters of the solar cells such as photovoltaic conversion efficiency, short circuit current, and fill factor strongly depend on the

Pc layer thickness. It was observed that the device with an 80 nm Zn_2Pc_2 layer exhibits the highest photovoltaic conversion efficiency, short circuit current, and fill factor. All these findings suggest that the performance of the ITO/ Zn_2Pc_2 / C_{60} /Al photovoltaic devices can be improved by optimization of the thickness of the Pc layer. It can be said that the Zn_2Pc_2 has good potential for photovoltaic applications.

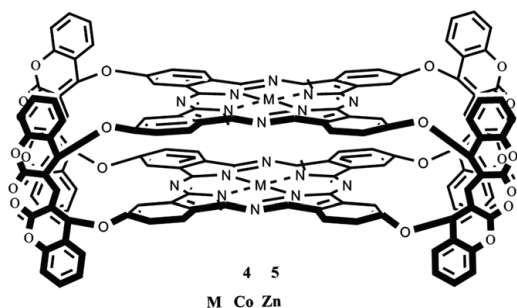


Figure 5. The structure of ball-type Pcs with 4 dicumaryl bridges.⁷⁴

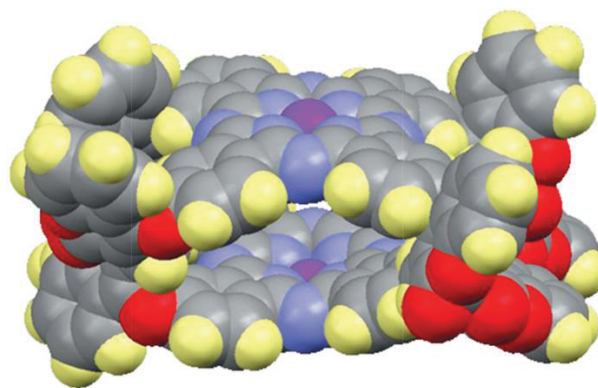


Figure 6. The space-filled structure of ball-type Pc given in Figure 5.⁷⁴

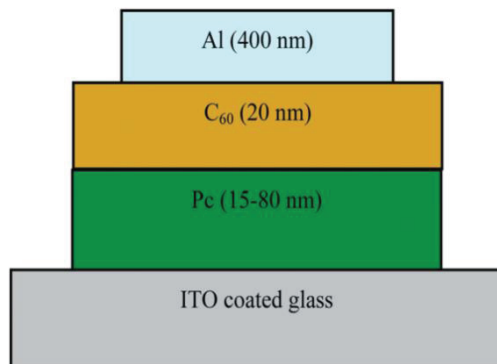
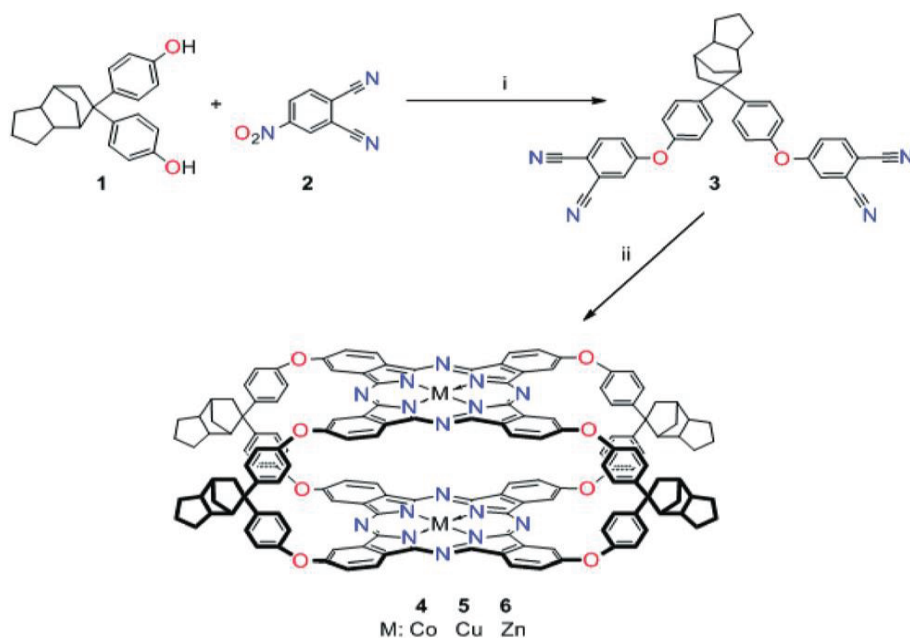


Figure 7. The composition of a photovoltaic device based on ball-type Pc of dicumaryl.⁷⁴

The electrochemical measurements of ball-type cobalt and zinc Pcs showed formation of electrochemically stable metal and ligand based mixed valence species, due to the intramolecular interactions between 2 MPc units. The high mixed valence splitting values indicated that the interactions between the 2 MPc units are remarkable; Co_2Pc_2 showed catalytic activity towards ORR in the acidic medium, as compared to Zn_2Pc_2 . This distinctive catalytic performance of cobalt Pc is attributed to the redox active behavior of the metal centers, enhancing the interaction with O_2 molecules. The ORR on a Co_2Pc_2 based catalyst occurs at relatively more positive potentials with lower over potentials, compared to some previously reported ball-type pentaerythritol-⁷⁵ and dithioerythritol-bridged⁷² Co_2Pc_2 based catalysts. In addition, it was found that the catalytic activity of a Co_2Pc_2 catalyst towards the ORR in the presence of methanol is better than that of a Pt-based one, indicating alternative direct methanol fuel cell (DMFC) applications.

[4,4'-(Octahydro-4,7-methano-5H-inden-5-ylidene)bisphenol] has been selected as another bridged compound to synthesize metallo ball-type Pcs. The results of the electrical, electrochemical, and electrocatalytic measurements of those novel ball-type Pcs indicated that this new type of Pc displays intriguing and extraordinary physicochemical properties. For instance, the ball-type cobalt Pc (Scheme 6)⁷⁶ displayed high catalytic

activity towards dioxygen reduction, presumably due to the presence of 2 interacting redox-active metal centers, the coordinating ability of the metal center for dioxygen, and the suitable distance between the 2 MPc units, which has vital importance in fuel cell applications (Figure 8). Furthermore, the combination of Au/Co₂Pc₂/p-Si was found to be a promising structure with a high dielectric constant and a low interface trap density suitable for metal-oxide-semiconductor (MOS) devices. It is well known that the overlap of the π -electron systems of neighboring molecules in the films of Pcs, depending on the film thickness and thus the stacking arrangement, the degree of crystallinity, and grain size, usually enhances their electrical properties. Therefore, it can be concluded from the outcomes of this study that the intriguing and extraordinary physicochemical properties of ball-type metal bisphthalocyanines can be attributed to the intermolecular interactions between neighboring molecules and/or the intramolecular interactions between the 2 face-to-face Pc rings and/or metal centers and in their films and/or solutions. These compounds have advantages in applications in various fields of technology such as fuel cells, optoelectronics, semiconductors, and sensors over the common mononuclear and noninteracting dinuclear Pcs.



Scheme 6. The synthesis of ball-type Pc bridges with [4,4'-(octahydro-4,7-methano-5H-inden-5-ylidene)bisphenol].⁷⁶

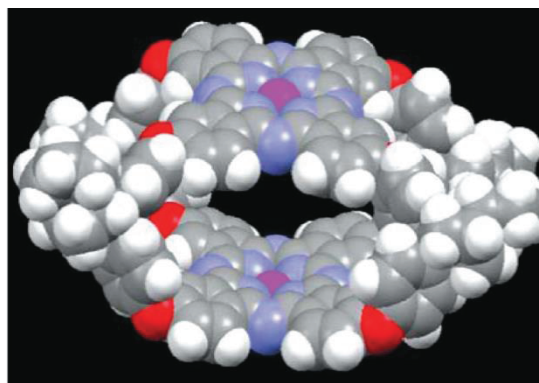
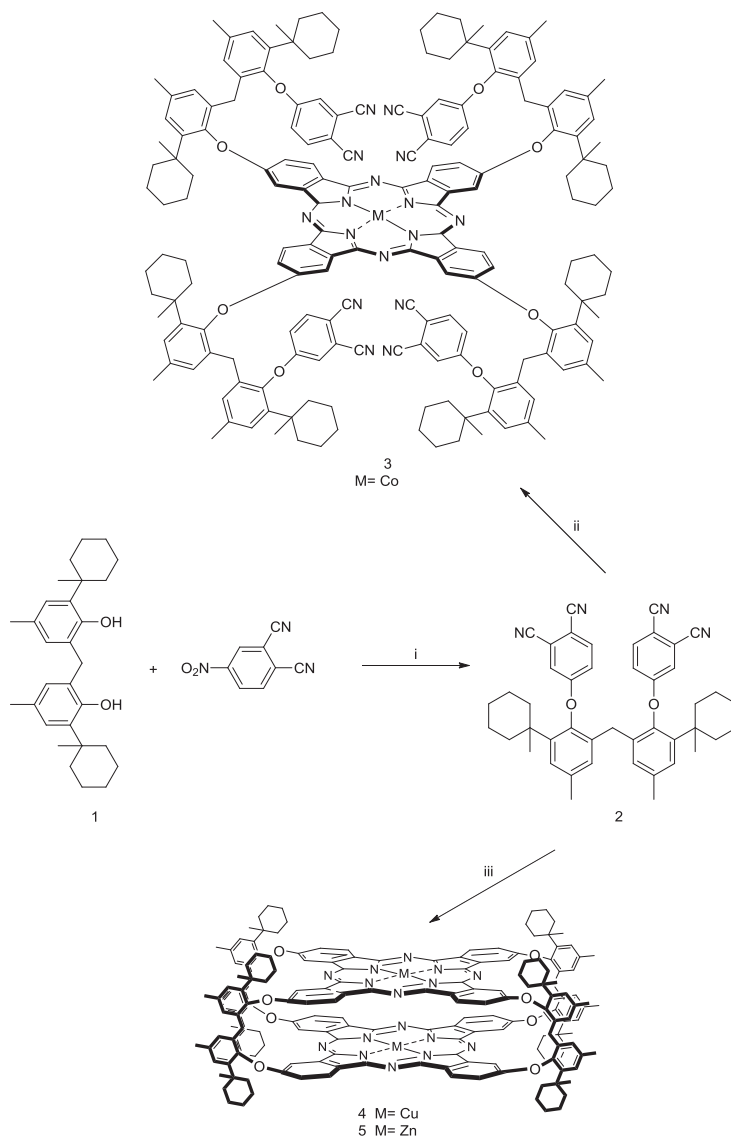


Figure 8. The space-filled structure of the ball-type Pc given in Scheme 6.⁷⁶

Starting from [bis[2-hydroxy-5-methyl-3-(1-methylcyclohexyl)phenyl]methane] as a bridged unit that was converted to nitrile with 4-nitrothalonitrile, further the reaction of dinitrile with metal salts in solid phase at 300 °C for 10 min gave ball-type Cu_2Pc_2 and Zn_2Pc_2 , but with cobalt salt in the same conditions only mono CoPc was obtained (Scheme 7).⁷⁷



Scheme 7. The synthesis of mono and ball-type Pcs with [bis[2-hydroxy-5-methyl-3-(1-methylcyclohexyl)phenyl]methane] used as bridged ligand.⁷⁷

The In dc conductivities of the films increase linearly with increasing temperature. This behavior of the In dc conductivity with temperature indicates that mono CoPc and ball-type Cu_2Pc_2 and Zn_2Pc_2 are semiconductors. Dc conductivity values of the film of Cu_2Pc_2 were found to be greater than those of the other films in the measured temperature range. The calculated activation energy values were found to be 0.70, 0.66, and 0.68 eV for the films of CoPc, Cu_2Pc_2 , and Zn_2Pc_2 , respectively. By examining the ac measurement results, the charge transport mechanism of the film of Cu_2Pc_2 can be modeled by single hopping all over the

measured frequency and temperature ranges. However, the charge transport mechanism for the films of CoPc and Zn_2Pc_2 can be interpreted in 2 parts. In the low temperature region the dominant conduction mechanism can be modeled by single hopping over the measured frequency range. In the high temperature region the dominant conduction mechanism for the films of CoPc and Zn_2Pc_2 can be modeled by small polaron tunneling (SP) in the low frequency region and by single hopping in the high frequency region. From impedance spectra results, it is observed that the bulk resistance of all the compounds decreases with increasing temperature, indicating semiconductor properties.

The electrochemical measurements of the binuclear ball-type complex Zn_2Pc_2 showed the formation of electrochemically stable ligand-based mixed-valence reduction species due to intramolecular interactions between the 2 Pc units and the delocalization of charge amongst the cofacial MPc units. The high mixed-valence splitting values for the redox couples of Zn_2Pc_2 showed that the interactions between the 2 MPc units in this complex are remarkable.

In recent years, considerable attention was given to the fabrication of molecular electronic devices based on phthalocyanine compounds and their derivatives. In a number of applications using molecular semiconductor thin films, the development of devices based on Pc films is dependent upon knowledge of the conduction mechanisms and the charge carrier mobility in these compounds. Determination of these parameters in those compounds plays an important role in decisions about the suitability of the material for a particular device application. The dc electrical properties of devices using various mono Pc thin film sandwich devices have been extensively studied in recent years,^{78,79} but relatively little work has been done on the dc behavior of ball-type Pcs.^{59,80}

In the case of ball-type Pcs, those substituents also have a bridged nature and change not only the symmetry of the face to face Pcs depending on the size of the molecule and the distance of between 2 Pcs, but also the properties of the compounds. Therefore, as a part of our systematic investigation, we selected the compound [pyridine-2,6-dimethoxy] with the electron donating and electron withdrawing properties as a peripheral and for bridging substituent between face to face Pcs (Scheme 8).⁸¹

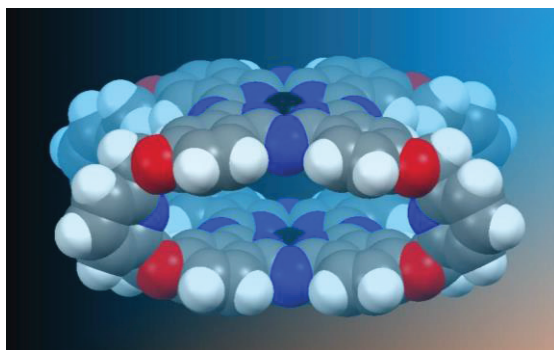
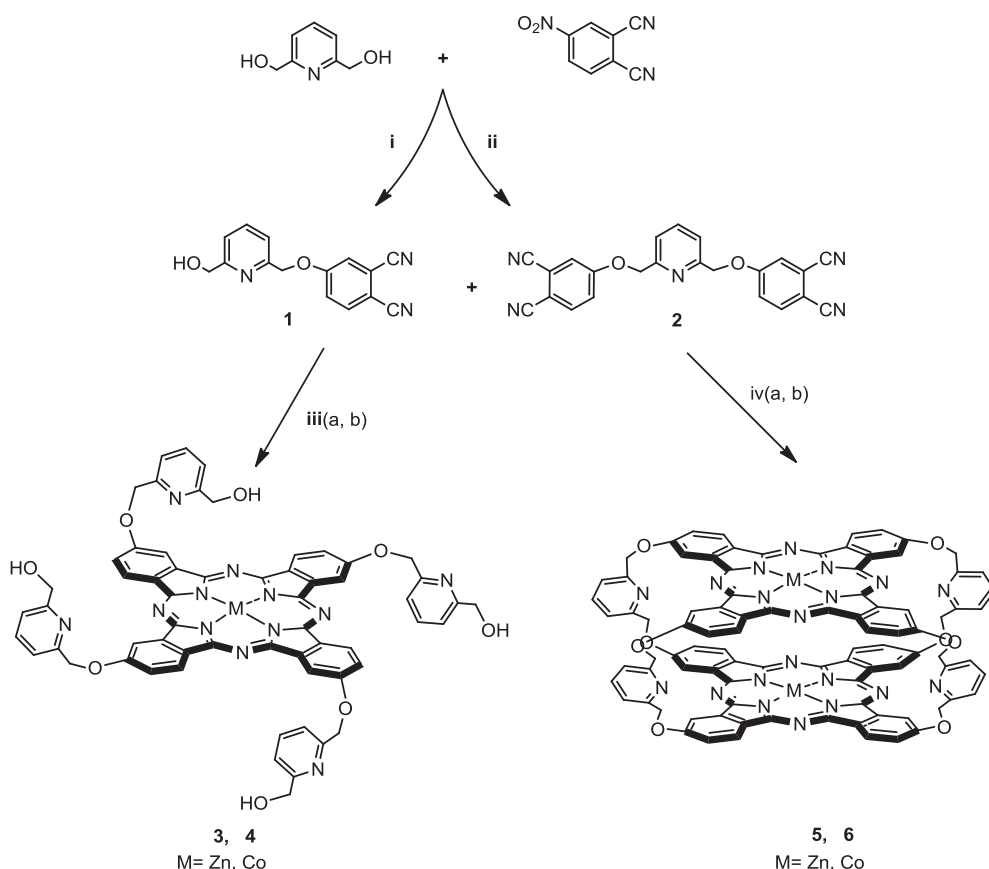


Figure 9. The space-filled structure of the ball-type Pc in Scheme 8.⁸¹

A sandwiched structure (Au/Pc/Ag) of mononuclear zinc, cobalt, and their ball-type counterparts has been fabricated (Figure 9) using silver as rectifying contacts and gold as ohmic contact. From the investigation of the current–voltage characteristics of the phthalocyanines, we reported that in the low voltage region the conduction mechanism is almost ohmic in nature, whereas at higher voltage the current transfer is space charged limited conduction. Various parameters, e.g., hole mobility, thermally generated hole concentrations, and trap density per unit energy range at the valence band edge, have been calculated. It has been observed that the ball-type Pcs have better electrical properties compared with the mono Pcs.

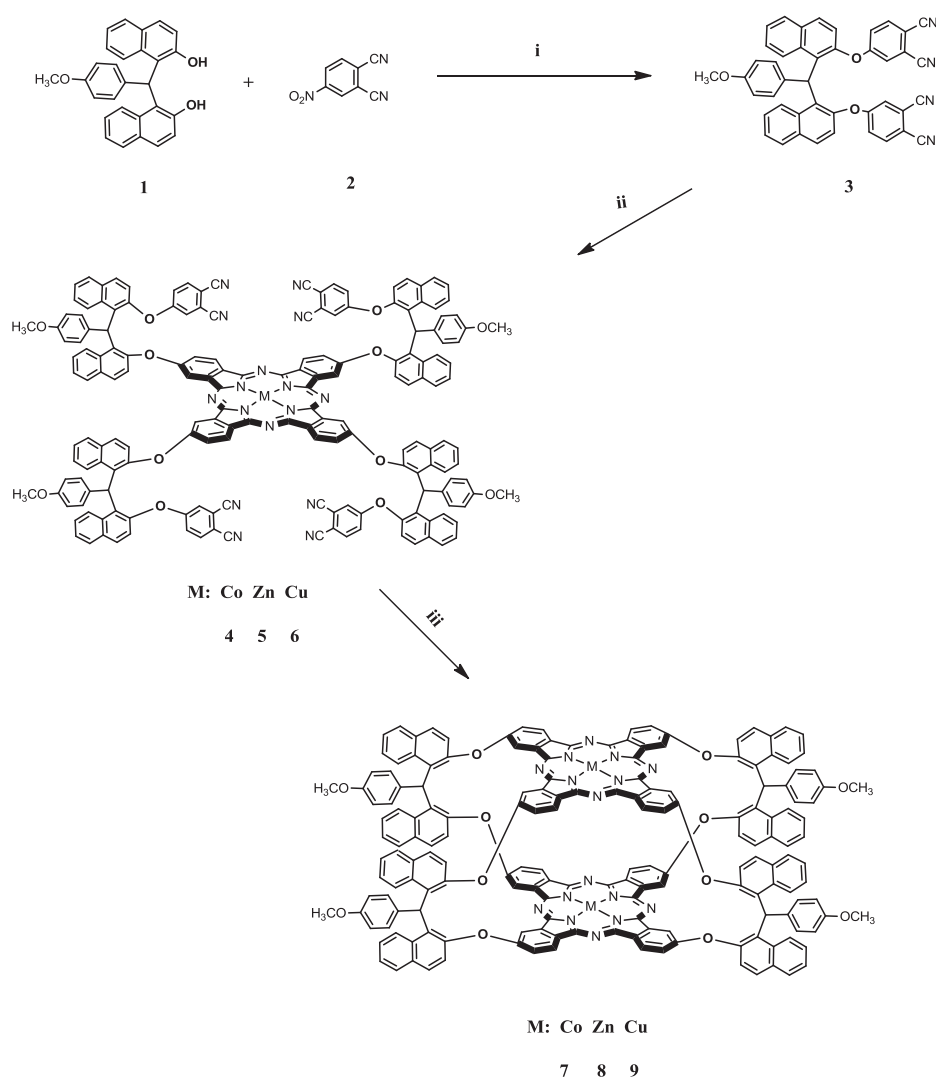


Scheme 8. The synthesis of mono and ball-type Pcs bridged 4 [pyridine-2,6-dimethoxy].⁸¹

[1,1'-p-Anisylidenbis(2-naphthoxyphthalonitrile)] was chosen as starting compound for ball-type Pc because of its poly benzene rings and expected rich electron donation structure. The ball-type Pcs, cobalt, zinc, and copper, have been obtained by 2-step reactions instead of 1. First nitrile, metal salt, in dimethylformamide (DMF) without additional catalysts heated under nitrogen in a sealed tube at 180 °C for 12 h gave only mono Pcs. In the second step, ball-type Pcs were obtained only by addition of excess metal salts to those mono Pcs under the same reaction conditions (Scheme 9).⁸² This is a very good opportunity not only to prepare mono metallo Pcs and homo metallo ball-type Pcs, but also hetero metallo ball-type Pcs, which are very important in many applications.

The comparison of the voltammetric behavior of the novel dinuclear ball-type Pcs Co_2Pc_2 , Zn_2Pc_2 , and Cu_2Pc_2 with their mononuclear homologues CoPc , ZnPc , and CuPc suggested that these compounds form Pc ring-based and/or metal-based mixed valence species as a result of the interactions between the 2 cofacial MPc units. Novel cobalt Pcs, mono and cobalt ball-type Pcs, displayed high catalytic activity towards dioxygen reduction. The high catalytic performance of these compounds was attributed to the redox-active nature of the cobalt metal center, which enhances the interaction with dioxygen. On the other hand, the further enhanced catalytic performance of Co_2Pc_2 in comparison with that of CoPc was attributed to its distinctive coordinating properties due to the presence of 2 interacting redox-active metal centers and thus its ability to bind dioxygen molecule through peroxo species, Co-O-O-Co , the promotion of the O-O bond breakage, and thus the increase in the tendency of reduction directly to water via the 4-electron path.

By choosing an appropriate metal electrode (drain and source electrode) high field effect mobility in organic field effect transistors (OFETs) consisting of spin-coated Co_2Pc_2 and Cu_2Pc_2 film was successfully demonstrated and characterized. It was observed that the field-effect mobility and the threshold voltage, which are the main OFET performance parameters, using spin-coated film of copper ball-type Pc as organic channels are much higher than the values of the respective devices using cobalt ball-type Pc and zinc ball-type Pc. One of the reasons why, unlike the ball-type Pc based OFETs, the mono-nuclear based OFETs are incapable of exhibiting a satisfactory saturation area of the drain current–drain voltage curves, is that in the film during the spin coating, stacking structures are rapidly formed. The results showed that ball-type films, especially copper ball-type Pc, are promising materials for the fabrication of OFETs with low threshold voltage and high mobility (Figures 10 and 11).⁸²



Scheme 9. The synthesis of mono and ball-type Pcs.⁸²

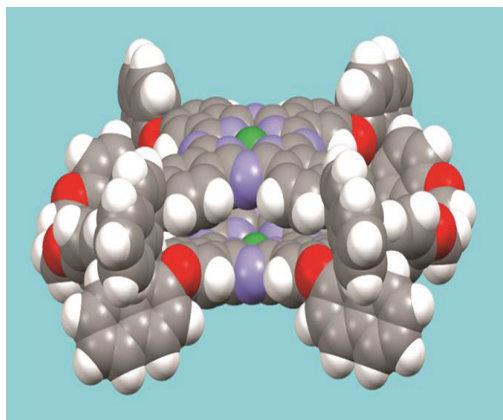


Figure 10. The space-filled presentation of the ball-type ZnPc given in Scheme 9.⁸²

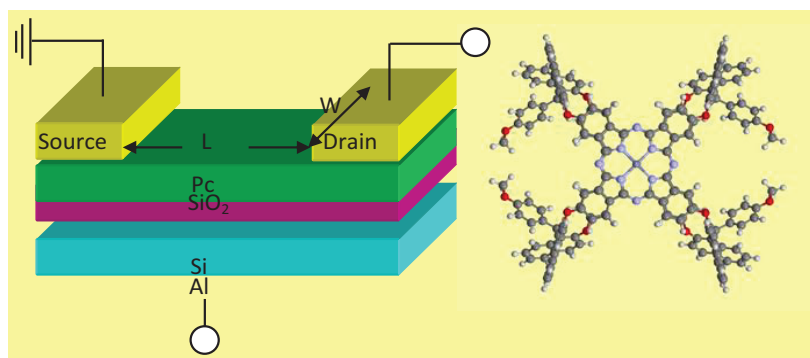


Figure 11. Configuration of OFET device based on ball-type Pcs (Co, Zn, Cu) given in Scheme 9.⁸²

3. Conclusions

We have summarized the historical development of Pcs in Turkey, emphasizing the ball-type Pcs, which are a new development in Pc chemistry in the last 10 years. This is quite an exciting development for the scientific community not only in Turkey but also the rest of the world.

To our knowledge, literature on this subject matter has been limited. Few papers have been seen in the literature for 10 years except ours, as far as we know. Unfortunately, the rare publications on that subject do not give us the opportunity to compare our results with those of others works. Therefore we can only refer to our papers published. Probably, this arises from finding a suitable compound for bridges, which are limited in the commercial catalogues, and to design and synthesize such compounds is a new research subject that needs more time and additional funding. Moreover the synthesized novel compounds are always not guaranteed to give ball-type Pcs.⁶⁰ However, the synthesis of ball-type Pcs is rather easy depending on the bridged compounds and metals used. In some cases all attempts result in mono Pcs, which should be further refluxed in a solvent using excess of metal salts (Scheme 9). However, this turns out to be an advantage for preparing hetero dinuclear ball-type Pcs as one can get different redox-active metal centers in the molecule like cobalt in one and copper in the other Pc ring. Depending on those different metal centers, electrical, electrochemical, photovoltaic, electronic, optoelectronic, gas-sensing, and nonlinear optic properties of ball-type Pcs change dramatically, because of interaction between redox centers and Pcs' macrocycles. Separation and purification of ball-type Pcs are in some cases easy, but can also be difficult, even tedious, like in other mono Pcs.⁵⁹

Unfortunately, industrial production of Pcs does not take place in Turkey. This, coupled with the fact that no company or private enterprise supports these scientists or exerts influence upon improvement in laboratories and commercializing the technology, means the work of Turkish scientists becomes more challenging. Regardless, we strongly encourage our scientists to work on this subject matter relentlessly. In particular, one may want to combine the Pcs with functional macromolecules, which we believe would demonstrate valuable properties. Lastly, don't forget, nothing is impossible in chemistry.

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