T.C.

YILDIZ TEKNİK ÜNİVERSİTESİ

FEN BİLİMLERİ ENSTİTÜSÜ

GÜNEŞ PİLİ UYGULAMALARI İÇİN YENİ BOYAR MADDELERİN SENTEZİ VE KARAKTERİZASYONU

Burak YILDIZ

DOKTORA TEZİ

Kimya Anabilim Dalı

Anorganik Kimya Programı

Danışman

Prof. Dr. M. Kasım ŞENER

Ağustos, 2022

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Burak YILDIZ tarafından hazırlanan tez çalışması 03.08.2022 tarihinde aşağıdaki jüri tarafından Yıldız Teknik Üniversitesi Fen Bilimleri Enstitüsü Kimya Anabilim Dalı, Anorganik Kimya Programı **DOKTORA TEZİ** olarak kabul edilmiştir.

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SİMGE LİSTESİ

λ	Dalga boyu
ε	Molar absorpsiyon katsayısı
°C	Santigrad

KISALTMA LİSTESİ

cm	Santimetre
DBU	1,8-Diazabisiklo[5.4.0]undek-7-en
DSSC	Boya duyarlı güneş pilleri
DMF	Dimetilsülfoksit
IR	Kızılötesi
M	Molarite
nm	Nanometre
NMR	Nükleer manyetik rezonans
PCE	Güç dönüşüm verimi
UV-vis	Morötesi-görünür bölge
THF	Tetrahidrofuran
TiO_2	Titanyumdioksit

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ÖZET

Güneş Pili Uygulamaları İçin Yeni Boyar Maddelerin Sentezi ve Karakterizasyonu

Burak YILDIZ

Kimya Anabilim Dalı

Doktora Tezi

Danışman: Prof. Dr. M. Kasım ŞENER

Boya esaslı güneş pilleri (DSSC), düşük üretim maliyeti, renk ve şeffaflık gibi ayarlanabilir estetik özelliklerinden dolayı önemli bir güneş enerjisi dönüştürme teknolojisidir. Boya esaslı güneş pillerinin temel bir bileşeni olan boya molekülü, solar fotonları toplar ve uyarılmış hale geçer. Uyarılan boya molekülü metal oksidin iletim bandına elektron enjekte ederek yük ayırma işlemini başlatır. Kırmızı/yakın kızılötesi bölgede soğurma yapması, termal ve kimyasal kararlılıkları nedeniyle ftalosiyaninler boya esaslı güneş pillerinde boya olarak kullanılmaktadır. Son yıllarda özellikle karboksilik asit içeren asimetrik ftalosiyaninler boya esaslı güneş pillerinde yaygın olarak kullanılmıştır. Karboksilik asit, boya molekülünün metal oksit yüzeyine tutunmasında işlev görmektedir. Bununla birlikte ftalosiyanin esaslı boyalar, metal oksidin yüzeyinden zamanla ayrılarak güneş hücrelerinin uzun süreli kararlılığını azaltmaktadır. Son yıllarda gerek güneş hücrelerinin uzun süreli kararlılığını,

gerek fotovoltaik performansını artırmak amacıyla boyanın metal oksidin yüzeyine tutunmasını sağlayacak karboksilik aside alternatif yeni fonksiyonel gruplar bulunmaya çalışılmaktadır. Bu tez, karboksilik aside alternatif olarak pirazol karboksilik asit içeren ve boya esaslı güneş pillerinde kullanılabilecek yeni asimetrik ftalosiyanin türevlerinin sentezlenmesini ve onların fotovoltaik özelliklerinin incelenmesini içeren üç farklı yayınlanmış çalışmadan oluşmaktadır.

Birinci çalışmada oksijen köprülü pirazol karboksilik asidin etil ester formundaki ftalonitril türevi ve 4-tersiyer bütil ftalonitril kullanılarak asimerik çinko ftalosiyanin sentezlenmiştir. Elde edilen ester formundaki çinko ftalosiyanin daha sonra hidroliz edilerek bağlayıcı grup olarak kullanılan pirazol karboksilik asit türevi sentezlenmiştir (**PCA-ZnPc-1**). Sentezlenen bileşiklerin yapıları spektroskopik yöntemlerle karakterize edilmiştir. İlgili bileşiğin boya duyarlı güneş pili (DSSC) uygulamaları yapılmış ve literatürdeki aynı yapıda olan ve bağlayıcı grup olarak karboksilik asit türevlerinin kullanıldığı asimetrik ftalosiyanin örneklerine göre yaklaşık 3 kat daha fazla bir güç dönüşüm verimliliği (PCE) elde edilmiştir. Bu artışın yanı sıra, elde edilen maksimum güç dönüşüm verimliliğine yarı iletken kaplı camın boyaya yalnızca 2 saat daldırılmasıyla ulaşılmıştır.

İkinci çalışmada bağlayıcı grup aynı olup asimetrik ftalosiyanin sentezinde 4-tersiyer bütil ftalonitril yerine periferal konumda 2 tane hekzil sülfanil grubu içeren ftalonitril türevi kullanılmıştır. Buradaki temel amaç hem S atomunun hem de elektron verici CH_2 gruplarının etkisiyle asimetrik ftalosiyaninin maksimum dalga boyunu kırmızıya kaydırarak güç dönüşüm verimliliği üzerindeki pozitif etkisinin ne kadar olacağını gözlemlemektir. Yapılan ölçümlerde 25 nm lik bir kırmızıya kayma tespit edilmiştir. İlgili bileşiğin boya duyarlı güneş pili uygulamasında 4-tersiyer bütil grubu taşıyan türevine göre güç dönüşüm verimliliğinde yaklaşık %30'luk bir artış gözlemlenmiştir. Bu çalışmada ayrıca fotoelektrokimyasal su ayrışması ile hidrojen üretimi ölçümleri yapılmıştır.

Üçüncü çalışmada da yine bağlayıcı grup aynı olup, asimetrik ftalosiyanin sentezinde bu sefer literatürde de birçok örneği bulunan ve hacimli grup kullanılmasıyla agregasyon azaltılarak güç dönüşüm verimliliğinde maksimum

değerlere ulaşılmış olması göz önünde bulundurularak periferal konumlarda hacimli 2,6-difenil fenol içeren ftalonitril türevi kullanılmıştır. Yeni bileşiklerin yapıları spektroskopik yöntemlerle aydınlatılmıştır. Güç dönüşüm verimliliği 4-tersiyer bütil grubu taşıyan asimetrik ftalosiyanin türevine göre yaklaşık %53, hekzil sülfanil grubu taşıyan türevine göre yaklaşık %18'lik bir artış göstermiştir.

Anahtar Kelimeler: Boya esaslı güneş pili, ftalosiyanin, pirazol karboksilik asit, bağlayıcı grup.

ABSTRACT

Synthesis and Characterization of New Dyestuffs for Solar Cell Applications

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Department of Chemistry

Doctor of Philosophy Thesis

Supervisor: Prof. Dr. M. Kasım ŞENER

Dye-sensitized solar cells (DSSCs) are an important technology for solar energy conversion due to their low production cost and adjustable esthetic properties such as color and transparency. The dye molecule, an essential component of dye-sensitized solar cells, collects solar photons and is excited. The excited dye molecule initiates the charge separation process by injecting electrons into the conduction band of the metal oxide. Phthalocyanines are used as dyes in dye-sensitized solar cells because of their absorption in the red/near-infrared region and their thermal and chemical stability. In recent years, asymmetric phthalocyanines containing carboxylic acid in particular have been used in dye-sensitized solar cells. The carboxylic acid ensures that the dye molecules adhere to the metal oxide surface. However, phthalocyanine-sensitized dyes detach from the metal oxide surface over time, which reduces the long-term stability of the solar cells. In order to increase the long-term stability and photovoltaic performance of solar cells, attempts have been made in recent years to find new functional groups as an alternative to carboxylic acid that allow the dye to adhere

to the metal oxide surface. This thesis consists of three different published studies, including the synthesis of new asymmetric phthalocyanine derivatives containing pyrazole carboxylic acid as an alternative to carboxylic acid that can be used in dye-sensitized solar cells and the study of their photovoltaic properties.

In the first study, asymmetric zinc phthalocyanine was synthesized using phthalonitrile derivatives of oxygen-bridged pyrazolecarboxylic acid in the form of ethyl ester and 4-*tert*-butylphthalonitrile. The obtained ester form zinc phthalocyanine was then hydrolyzed, and the pyrazolecarboxylic acid derivative used as an anchor group was synthesized (**PCA-ZnPc-1**). The structures of the synthesized compounds were characterized by spectroscopic methods. Dye-sensitized solar cells (DSSCs) were used with the appropriate compound, and a power conversion efficiency (PCE) of about three times was obtained compared to the asymmetric phthalocyanine samples in the literature, which have the same structure and use carboxylic acid derivatives as the anchor group. Besides this increase,the maximum power conversion efficiency was achieved by immersing the semiconductor coated glass in the dye solution for only 2 hours.

In the second study, the same anchor group was used, but instead of 4-*tert*-butylphthalonitrile, a phthalonitrile derivative with two hexylsulfanyl groups in the peripheral position was used. The main purpose was to observe how positively the asymmetric phthalocyanine affects the energy conversion efficiency by shifting the maximum wavelength of the asymmetric phthalocyanine due to the effect of the S atom and the electron donating CH_2 groups. A red shift of 25 nm was observed in the measurements. When the related compound was applied in dye-sensitized solar cells, an increase in the energy conversion efficiency of about 30 % was observed compared to the derivative with the 4-*tert*-butyl group. In addition, measurements of hydrogen production by photoelectrochemical water splitting were performed in this study.

In the third study, the linking group was the same, and a phthalonitrile derivative containing bulky 2,6-diphenylphenol in the peripheral positions was used in the synthesis of the asymmetric phthalocyanine, since there are many examples of this in the literature and the maximum energy conversion efficiency was achieved by

reducing aggregation through the use of bulky groups. The structures of the new compounds were characterized by spectroscopic methods. The energy conversion efficiency of the phthalocyanine compound increased by about 53 % compared to the asymmetric phthalocyanine derivative with the 4-*tert*-butyl group and by about 18% compared to the derivative with the hexylsulfanyl group.

Keywords: Dye-sensitized solar cell, phthalocyanine, pyrazole carboxylic acid, anchoring group.

1
GİRİŞ

1.1 Tezin Amacı ve Kapsamı

Günümüzde, boya duyarlı güneş pilleri (DSSC'ler), mevcut silikon güneş pillerine en güçlü alternatiflerden biridir. DSSC'lerin ana bileşenleri boya molekülü ve yarı iletken metal oksit nano parçacıklarından oluşan çalışma elektrodu, redoks elektrolit ve karşıt elektrottur. Son 10 yılda, boya molekülü, elektrotlar ve elektrolit gibi DSSC'nin çeşitli bileşenlerinin güneş ışığını foto-akıma dönüştürme performansı üzerindeki etkisiyle ilgili çok sayıda araştırma gerçekleştirilmiştir. Özellikle, en büyük çaba güneş ışığının absorpsiyonundan ve metal oksidin iletim bandına elektron enjeksiyonundan sorumlu DSSC'lerin anahtar bileşeni olan yeni boya moleküllerinin tasarımına gösterilmiştir [1]. Organik boya molekülleri genellikle elektron verici-aracı-alıcı/bağlayıcı (D-π-A) yapısına sahip "push-pull" sistemleri olarak tasarlanmaktadır. Önemli bir makrosiklik tetrapirol türevi olan ftalosiyaninler 18-π elektron sistemine sahip olmaları, kırmızı/yakın kızılötesi bölgede soğurma yapmaları, termal ve kimyasal kararlılıkları nedeniyle DSSC'lerde boya olarak kullanılmaktadır. Boya moleküllerinde alıcı/bağlayıcı grup, metal oksit yarı iletkenine elektron enjeksiyonunu sağlayan ve boyanın metal oksit yüzeye tutunmasında işlev gören başlıca fonksiyonel gruplardan biridir. DSSC'ler için en tipik bağlayıcı gruplar karboksilik asit ve siyanoakrilik asit grupları gibi görünse de, son otuz yılda çeşitli geleneksel olmayan bağlayıcı gruplar geliştirilmiş ve rapor edilmiştir. Bu bağlayıcı gruplara örnek olarak piridin, 8-hidroksikinolin gibi heterosiklik ligandlar örnek olarak verilebilir. Bu heterosiklik ligandlar metal oksit yüzeyi ile koordinasyon bağı oluşturabilir. Koordinasyon bağı oluşumunun elektron enjeksiyon verimini artırdığı ve N-donör ligandın metal oksit yüzeyin farklı uçlarına adsorbe olduğu gösterilmiştir [2].

Önemli bir heterosiklik ligand olan pirazol karboksilik asit, pirazol halkası üzerinde iki N-donörü ve karboksilat üzerinde iki O donörüne sahiptir ve metal iyonları ile kararlı kompleksler oluşturabilir [3]. Ayrıca pirazol halkası elektron

çekici bir gruptur [4]. Pirazol karboksilik asidin metal iyonları ile kararlı şelat oluşturması [5] ve elektron çekici özelliği göz önünde bulundurularak bu tez kapsamında tarafımızdan ilk defa bağlayıcı grup olarak pirazol karboksilik asit içeren asimetrik çinko ftalosiyaninler **PCA-ZnPc-1-3** sentezlenmiş ve fotovoltaik özellikleri incelenmiştir [6]–[8].

1.2 Orijinal Katkı

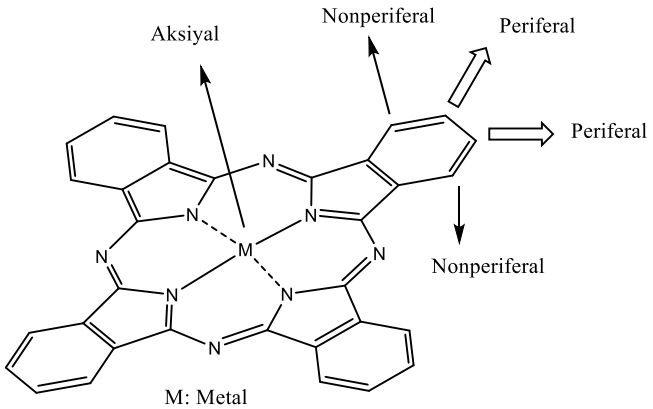
Bu tez kapsamında karboksilik asit bağlayıcı grubuna alternatif olabilecek ve literatürde boya esaslı güneş pillerinde ilk defa bağlayıcı grup olarak kullanılan pirazol karboksilik asit içeren yeni asimetrik çinko ftalosiyaninler sentezlenmiştir. Yapılan fotovoltaik ölçümler sonucunda da karboksilik asit bağlayıcı grubuna göre üstünlükleri sonuçlarla belirtilmiş ve literatürde yeni bir bağlayıcı grup olarak yerini almıştır.

Tez kapsamında yayınlanan 3 çalışmada da aynı bağlayıcı grup kullanılmış, sadece asimetrik ftalosiyanin yapısında bulunan diğer sübstitüentler değiştirilerek güç dönüşüm verimliliğinin artırılması başarılmıştır.

2
LİTERATÜR ÖZETİ

2.1 Ftalosiyaninler

Ftalosiyaninler yakın IR bölgede kuvvetli absorpsiyon yapmalarını sağlayan delokalize 18-π elektronuna sahip termal ve kimyasal olarak kararlı iki boyutlu tetrapirolik makrosikliklerdir. Ftalosiyaninler kuvvetli Soret ve Q bandları, yaklaşık 300.000 M^{-1} cm^{-1} lik molar absorptivite katsayıları ve yüksek floresans kuantum verimleri nedeniyle ideal ışık absorplayıcı özelliğe sahiptirler [9]. Q bandı ftalosiyanin türevinin simetrisine göre tek ya da ikiye yarılmış halde olabilir ve band genişliği bağlanan farklı sübstitüentlerle kaymalar gösterebilir. Ftalosiyaninlerin güçlü absorpsiyon karakteristiği yanında, sayısız birçok özelliği de ftalosiyaninlerin konjuge aromatik kromoforik yapısından kaynaklanmaktadır. Bu yapısal özellikleri onları farklı teknolojik alanlarda kullanılan yeni moleküler malzemeler için yapı taşı haline getirmiştir [10]–[12]. Ek olarak metal merkezleri, periferal, non-periferal ve aksiyal konumlarına farklı sübstitüent eklenebilmesi nedeniyle zengin redoks kimyasına sahiptirler (Şekil 2.1).



Şekil 2. 1 Ftalosiyaninlerin periferal, nonperiferal ve aksiyal konumları

Bu kırmızı ve yakın kızılötesi bölge pigmentlerinin fiziksel ve optik özellikleri onları organik elektronikler [10]–[12], fotovoltaikler [13]–[16], katalizörler [17]

ve fotodinamik terapi [18] gibi uygulama alanlarında kullanılabilmeleri için mükemmel bir aday yapar.

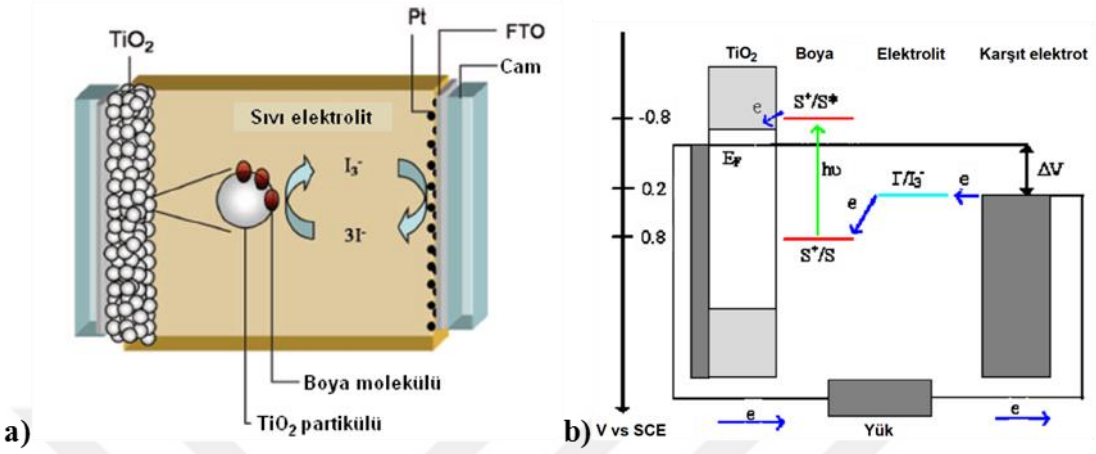
2.2 Boya Duyarlı Güneş Pilleri (DSSC)

Boya duyarlı güneş pilleri ilk olarak 1991 yılında O'Regan ve Gratzel tarafından tanıtılmıştır [19]. Bu atılımdan önce de geniş bant aralıklı yarı iletkenlerin boya duyarlılığı öngörülmüştür ve bazı girişimler rapor edilmiştir. Ancak yarı iletkenin düz yüzeyinin sadece tek katman boyanın adsorplanmasına izin vermesine ve yeterli ışık absorpsiyonunun sağlanamamasına bağlı olarak verimlilik sürekli düşük kalmıştır [20], [21]. Farklılaşan bu yapının önceki girişimlere göre iki önemli yeniliği vardır. Bunlardan birincisi yarı iletkenin yüzeyinin pürüzlülüğünden kaynaklanan daha fazla boyanın yüzeye adsorbe olabilmesi ve ışık absorpsiyonun da artmasıdır. İkinci yenilik ise bu deneysel şartlar altında elde edilen kararlı ve sağlam yeni boyalardır. Temel olarak malzeme saflığı standartlarının düşük olması nedeniyle bu hücreler düşük üretim maliyetleri ve düşük enerji harcamalarıyla öne çıkmaktadırlar. Proses için vakum ya da yüksek sıcaklık gerekli değildir. Bütün bu özellikleri onları standart silikon fotovoltaiklerin umut verici alternatifi haline getirmektedir.

2.3 Boya Duyarlı Güneş Pillerinde Çalışma Prensibi

Şekil 2.2 boya duyarlı TiO_2 güneş pilinin yapısı ve pilde gerçekleşen elektron alışverişini göstermektedir. DSSC' lerin çalışma prensibinde, ışığın yarı iletken TiO_2 üzerine adsorplanmış olan boya olarak kullanılan bileşikler tarafından absorplanması sonucunda başlamaktadır. Işığı absorplayan boya uyarılmış hal enerji seviyesine geçmektedir. Uyarılan boya molekülünden bir elektron TiO_2' nin iletkenlik bandına geçmektedir. İletkenlik bandına geçen elektronlar, TiO_2 filmindeki nano kristal yapı üzerinden saydam elektroda varmakta, daha sonra ise dış devreye ilerlemektedir. Bir elektronunu titanyum dioksidin iletkenlik bandına vermesiyle meydana gelen boya katyonları kullanılan elektrolit ile tekrar nötral hale getirilmektedir. Yükseltgenmenin olduğu elektrolit ise platin kaplı elektroda dış devreden ulaşan elektron tarafından indirgenmektedir [22]. Bu şekilde organik boya duyarlı güneş pilinin çalışması sırasında net yük her zaman sıfırdır ve kimyasal olarak bir değişme meydana gelmemektedir. Bu elektron alışverişleri

ile foto-akım meydana gelmektedir. Organik boya duyarlı güneş pilinde bu akımın devamlı hale getirilebilmesi için indirgenme-yükseltgenme tepkimelerinin devamlı olması gerekmektedir [22], [23].



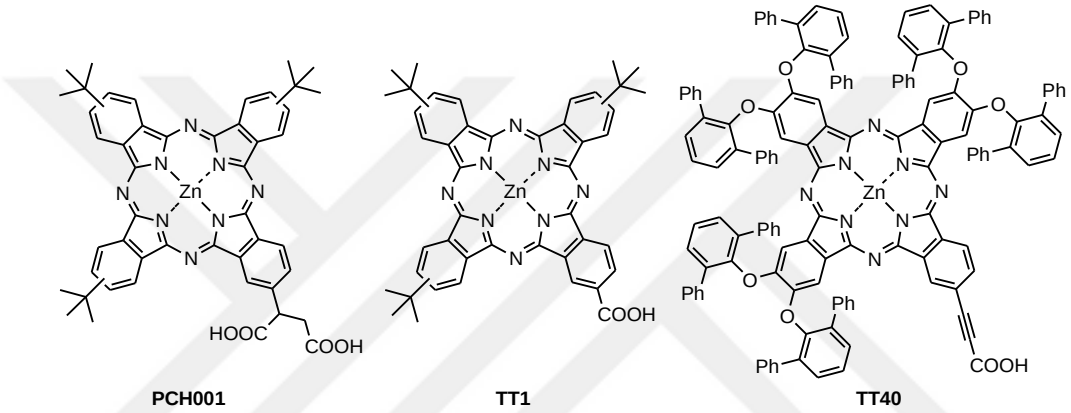
Şekil 2. 2 Boya esaslı TiO_2 güneş pilinin **a)** yapısı **b)** çalışma prensibi [22], [23].

2.4 Asimetrik Ftalosiyanin Esaslı Boyalar

Gratzel ve arkadaşları tarafından 1999 yılında yayınlanan makale boya duyarlı güneş pillerinde kullanılacak ftalosiyaninlerin moleküler tasarımında yeni araştırma alanları için dönüm noktası olmuştur [9]. Bu çalışmada boya duyarlı güneş pillerinde kullanılmak üzere sentezlenen bazı simetrik ftalosiyaninlerin yanında, periferal pozisyonda hacimli tersiyer bütil grupları içeren asimetrik ftalosiyaninlerin de fotovoltaik performansları rapor edilmiştir [9]. Yayınlanan bu makalede kullanılan simetrik ftalosiyaninlerin agregasyonlarının yüksek olduğu, bu sebeple sistem veriminin düştüğü ve bu verimin artırılabilmesi amacıyla agregasyonlarının bir miktar engellenebilmesi için bazı agregasyon engelleyici maddelerin kullanılması gerektiği belirtilmiştir. Bunun yerine hacimli tersiyer bütil grupları kullanılarak hazırlanan asimetrik ftalosiyanin türevlerinde hem organik çözücülerde çözünmenin arttığı hem de agregasyonun simetrik ftalosiyanin türevlerine göre azaldığı gözlemlenmiştir. Bu ilk bilgiler ışığında boya duyarlı güneş pillerinde asimetrik ftalosiyanin türevleri kullanımına ilgi artmıştır.

Özellikle, Nazeeruddin ve arkadaşları tarafından 2007 yılında gerçekleştirilen AB_3 tipi asimetrik karboksilik asit sübstitüe çinko ftalosiyaninlerin (**PCH001** ve **TT1**)

sentezi ve DSSC'lerde boya molekülü olarak kullanımıyla ilgili çalışmalardan sonra birçok araştırma grubu ftalosiyanin duyarlı güneş pilleri alanına yoğunlaşmıştır [15], [24], [25] (Şekil 2.3). Elektron verici *tert*-bütil grupları (B) ve elektron çekici ve aynı zamanda bağlayıcı karboksilik asit grubu (A) içeren AB_3 tipi asimetrik çinko ftalosiyanin boyaları kullanılarak % 4,1'e kadar fotovoltaik performansa ulaşılmıştır [26]. *Tert*-bütil grupları yerine farklı elektron verici gruplar içeren AB_3 tipi asimetrik çinko ftalosiyaninler **PcS20** ve **TT40** ile ftalosiyanin esaslı güneş pillerinde en yüksek güç verimi olan % 6,4'e ulaşılmıştır [9].



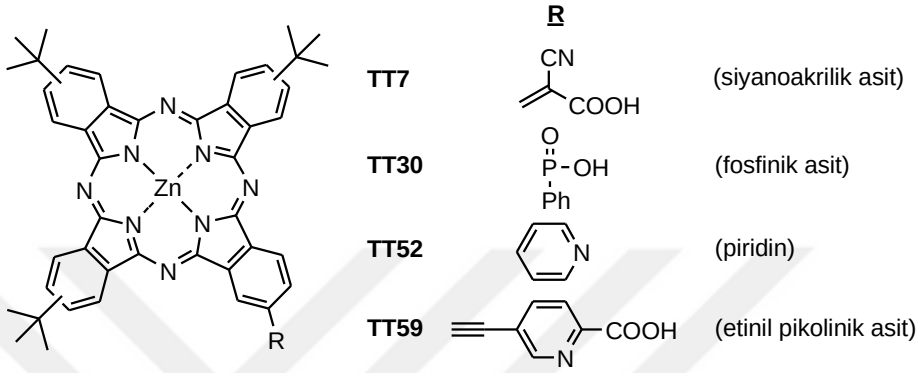
Şekil 2. 3 PCH001, **TT1** ve **TT40** boyalarının yapısı

2.5 Boya Duyarlı Güneş Pillerinde Kullanılan Bağlayıcı Gruplar

Karboksilik asit grubu, boya molekülünün metal oksit yüzeyine tutunmasında işlev görmektedir. Karboksilik asit için altı muhtemel bağlanma modu tanımlanmasına rağmen, bidentat modları (şelat ve köprü modları) olan yapılar genellikle diğerlerine kıyasla üstün stabilite sergilemektedir [27]. Bununla birlikte makrosiklik tetrapirol esaslı boyalar, metal oksidin yüzeyinden zamanla ayrılarak fotonları elektrona dönüştürme kapasitelerini kaybetme ve güneş hücrelerinin uzun süreli kararlılığını azaltma eğilimindedirler [28].

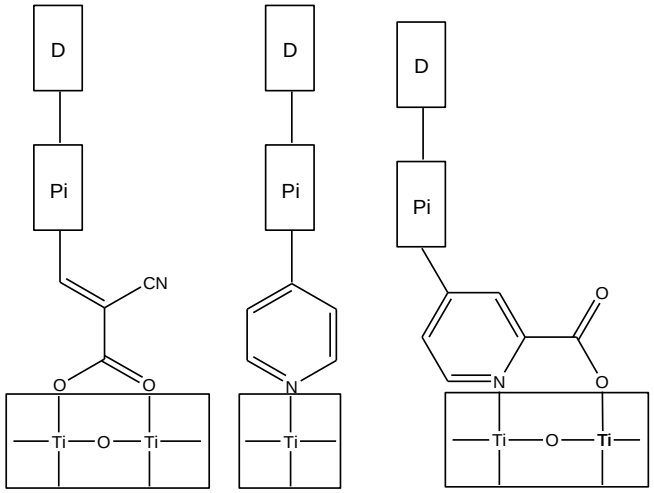
Son yıllarda gerek güneş hücrelerinin uzun süreli kararlılığını, gerek fotovoltaik performansını artırmak amacıyla boyanın metal oksidin yüzeyine tutunmasını sağlayacak karboksilik aside alternatif yeni bağlayıcı gruplar bulunmaya çalışılmaktadır [15], [27] (Şekil 2.4). DSSC'lerde karboksilik asitten sonra yaygın olarak kullanılan diğer bir bağlayıcı/alıcı grup olan siyanoakrilik asidin ışık altında

ve eser miktarda su varlığında fotovoltaik hücre içerisinde istenmeyen retro aldolik bozunma reaksiyonuna uğrayabileceği gösterilmiştir ve bu durum cihazın ömrünü olumsuz yönde etkileyebilmektedir. Sadece piridin alıcı/bağlayıcı grubuna sahip boyaların fotovoltaik verimleri genellikle orta düzeyde iken yük enjeksiyon verimlerinin karboksilik asit alıcı/bağlayıcı gruba sahip benzer boyalar ile aynı olduğu görülmüştür.



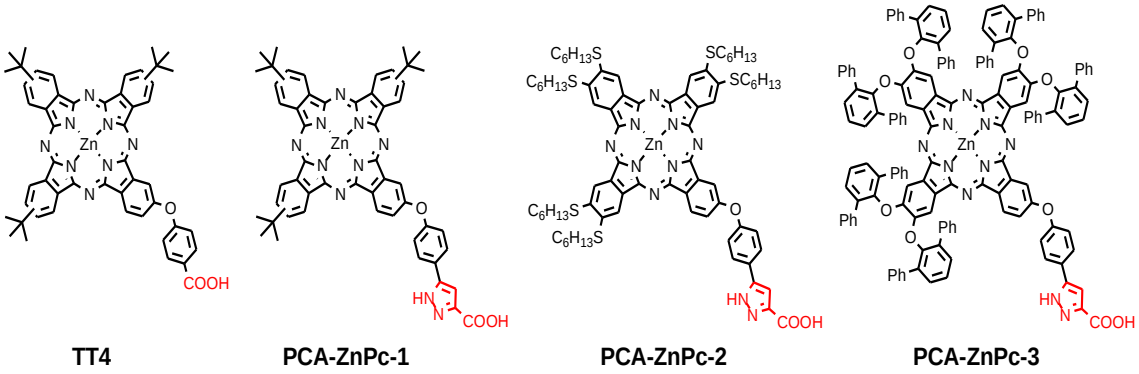
Şekil 2. 4 Farklı bağlayıcı gruplar içeren ftalosiyanin boyaları

Şekil 2.5'te görüldüğü gibi piridin alıcı/bağlayıcı grubuna sahip boyanın, Lewis asidik titanyum bölgelerinin piridin azotuyla koordinasyonu ile TiO_2 yüzeyine bağlandığı bildirilmiştir. Reginato ve arkadaşları özellikle pikolinik asit gibi hem karboksilik asit hem piridin halkası ihtiva eden bağlayıcı grupların kararlı ve yüksek performansa sahip yeni nesil DSSC'lerin hazırlanmasındaki önemine dikkat çekmişlerdir. Pikolinik asit grubu titanyum oksit yüzeye hem piridin azotu hem de karboksilik asit üzerinden bağlanmaktadır [29].



Şekil 2. 5 Siyanoakrilat, piridin ve pikolinik asit alıcı/bağlayıcı gruplarının titanyum okside bağlanma modları

Pirazol karboksilik asit, pirazol halkası üzerinde iki N-donörü ve karboksilat üzerinde iki O donörüne sahiptir ve metal iyonları ile kararlı kompleksler oluşturabilir [3], [30], [31]. Ayrıca pirazol halkası elektron çekici bir gruptur [4]. Pirazol karboksilik asidin metal iyonları ile kararlı şelat oluşturması [5] ve elektron çekici özelliği göz önünde bulundurularak yakın zamanda tarafımızdan D-π-A (örneğin *tert*-bütil grupları-çinko ftalosiyanin-pirazol karboksilik asit, **PCA-ZnPc-1**) yapısında asimetrik çinko ftalosiyaninler **PCA-ZnPc-1** [6], **PCA-ZnPc-2** [7], **PCA-ZnPc-3** [8] sentezlenmiş ve fotovoltaik özelikleri literatürdeki benzerleriyle karşılaştırılmıştır (Şekil 2.6).



Şekil 2. 6 TT4 ve **PCA-ZnPc-1-3** boyalarının yapıları

3
FTALOSİYANİN ESASLI GÜNEŞ PİLLERİ İÇİN YENİ BİR BAĞLAYICI GRUP PİRAZOL 3-KARBOKSİLİK ASİT

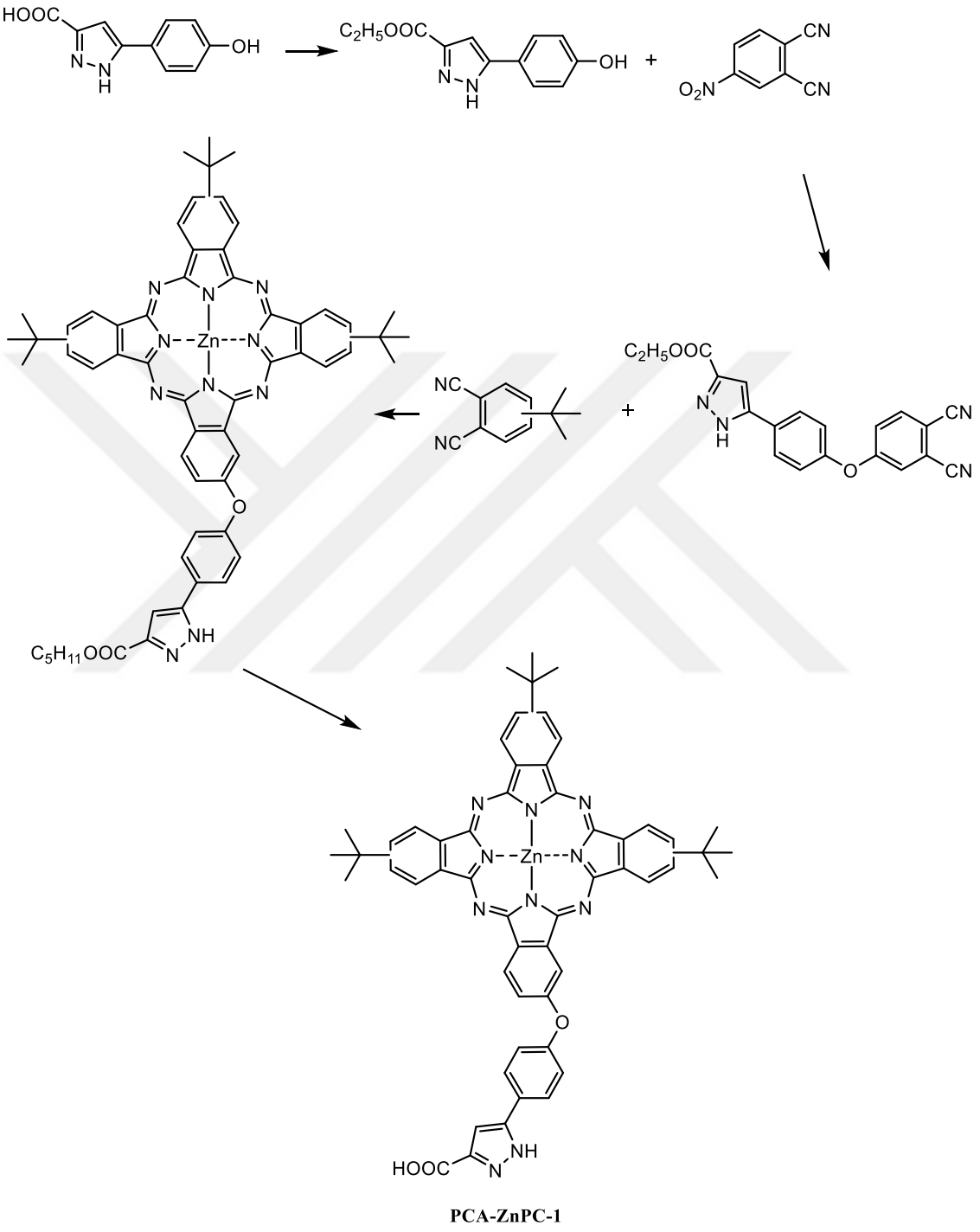
Güneş Enerjisi, sayı 174, pp. 527–536, 2018.

Bu çalışmada boya duyarlı güneş pillerinde kullanılmak amacıyla elektron verici üç tersiyer bütil grubu ve elektron çekici pirazol-3-karboksilik asit bağlayıcı grubu içeren yeni asimetrik çinko ftalosiyanin sentezlenmiştir. İlk olarak Fischer esterleşme metodu kullanılarak 3-(4-hidroksifenil)-1H-pirazol-5-karboksilik asit bileşiği H_2SO_4 ve etanol varlığında ester formuna dönüştürülmüştür. Daha sonra bu bileşik DMF içerisinde K_2CO_3 varlığında 4-nitro ftalonitrille reaksiyona sokularak 5-[4-(3,4-disiyanofenoksi)-fenil]-1H-pirazol-3-karboksilik asit etil ester elde edilmiştir.

Sentezlenen ftalonitril türevi ticari olarak bulunan 4-tersiyer bütil ftalonitril ile istatistiksel kondenzasyon metoduna göre $Zn(CH_3COO)_2$ ve DBU varlığında pentanol içerisinde reaksiyona sokularak ester formunda asimetrik çinko ftalosiyanin sentezlenmiştir. Bu reaksiyon şartlarında transesterifikaskon meydana gelmiş, bileşiğin yapısı etil ester formundan pentil ester formuna dönüşmüştür. Gerekli saflaştırma işlemlerinden sonra ester halindeki ftalosiyanin türevi NaOH çözeltisi varlığında THF içerisinde hidroliz edilerek hedeflenen bağlayıcı pirazol-3-karboksilik asit grubu taşıyan asimetrik çinko ftalosiyanin elde edilmiştir. Yeni bileşiklerin yapıları IR, Kütle, ^{1}H- NMR, ^{13}C-NMR, UV-Vis, X-Ray kristallografisi gibi spektroskopik yöntemlerle karakterize edilmiştir.

Hedeflenen bileşiğin sentezi sonrasında teorik hesaplama çalışmaları ve boya duyarlı güneş pili ölçümleri gerçekleştirilmiştir. Bileşiğin boya duyarlı güneş pili ölçümü sonucunda ilk olarak güç dönüşüm verimliliği % 1,29 elde edilmiştir. Agregasyonu kırıcı yardımcı adsorbent CDCA eklenmesi ile ise güç dönüşüm verimliliği % 1,74'e yükselmiştir. Karboksilik asit bağlayıcı grubu taşıyan benzer

örneklerine göre güç dönüşüm verimliliğinin yaklaşık olarak 3 kat daha fazla olduğu tespit edilmiştir.



PCA-ZnPC-1

Şekil 3. 1 PCA-ZnPc-1 sentez şeması

4

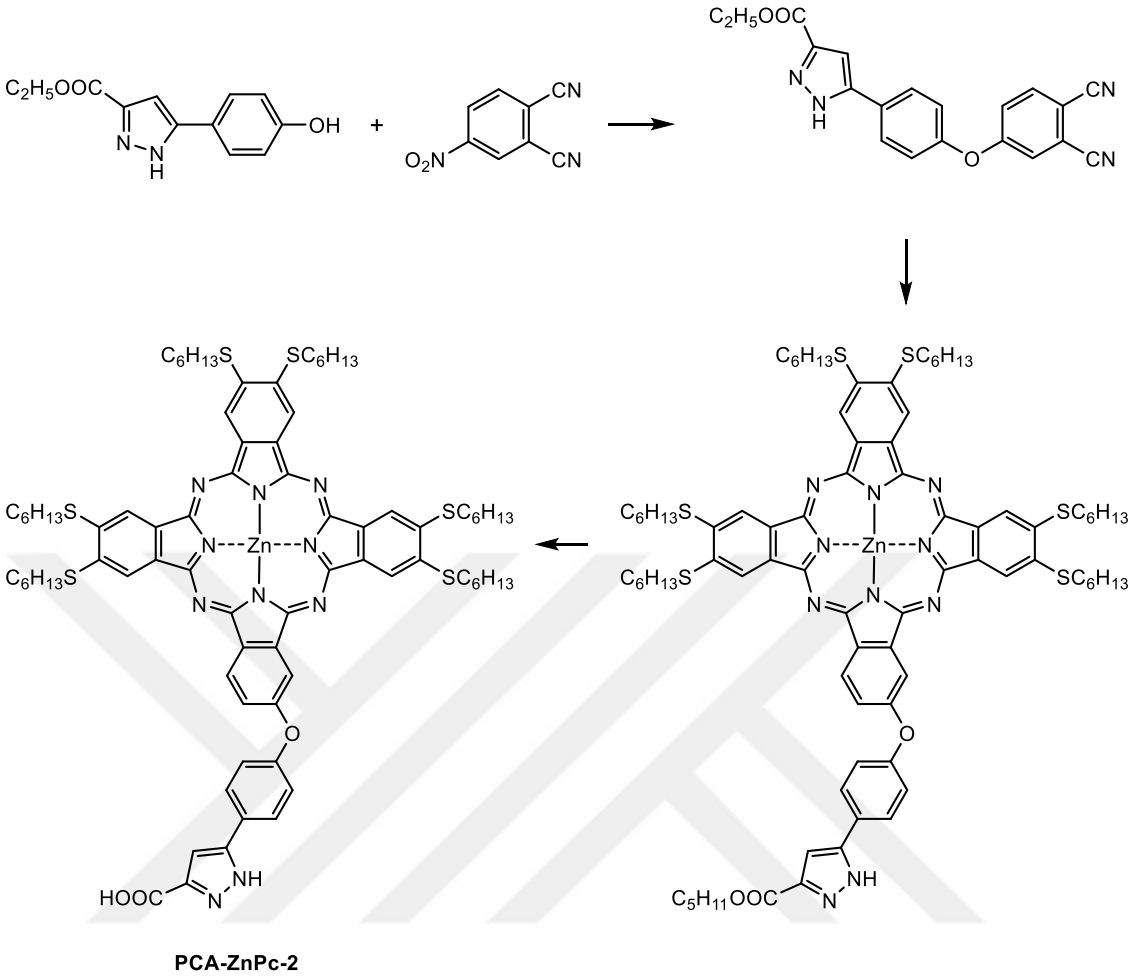
FOTOELEKTROKİMYASAL SUYUN AYRIŞMASINDA VE BOYA DUYARLI GÜNEŞ PİLLERİNDE KULLANILAN PİRAZOL-3-KARBOKSİLİK ASİT SÜBSTİTÜE ASİMETRİK FTALOSİYANİN İÇEREN FOTOANOTLAR

Güneş Enerjisi, sayı 191, pp. 654–662, 2019.

Bu çalışmada agregasyonu engelleyici ve elektron verici hacimli alifatik gruplar kullanılarak **PCA-ZnPc-1** molekülünde elde edilen güç dönüşüm verimliliğini daha yüksek değerlere çıkarmak amacıyla periferal konumda altı tane hekzil sülfanil grubu ve bir tane pirazol-3-karboksilik asit bağlayıcı grubu içeren asimetrik çinko ftalosiyanin sentezlenmiştir. İlk olarak bir önceki kısımda sentez yöntemi ayrıntılı olarak anlatılan 5-[4-(3,4-disiyanofenoksi)-fenil]-1H-pirazol-3-karboksilik asit etil ester tekrar sentezlenmiştir. Daha sonra 4,5-bis(hekziltiyo) ftalonitril bileşiği literatüre göre sentezlenmiştir [32]. Bu iki ftalonitril türevinin $Zn(CH_3COO)_2$, DBU varlığında pentanol içerisindeki reaksiyonu sonucunda ester formunda asimetrik çinko ftalosiyanin bileşiği elde edilmiştir. Bu bileşikte de reaksiyon sonucunda etil ester formu pentil estere dönüşmüştür. Ester yapısı NaOH çözeltisi ve THF karışımında hidroliz edilerek hedeflenen bağlayıcı pirazol-3-karboksilik asit içeren asimetrik çinko ftalosiyanin (**PCA-ZnPc-2**) elde edilmiştir. Yeni bileşiklerin yapıları IR, Kütle, ^{1}H- NMR, ^{13}C-NMR, UV-Vis gibi spektroskopik yöntemlerle karakterize edilmiştir.

Elde edilen bileşiğin boya duyarlı güneş pili ölçümlerinde yardımcı adsorbent kullanılmadan güç dönüşüm verimliliği % 1,67, yardımcı adsorbent (CDCA) kullanılarak güç dönüşüm verimliliği % 1,89 olarak bulunmuştur.

Bu çalışmada ayrıca **PCA-ZnPc-2** molekülünün boya duyarlı fotoelektrokimyasal hücre ile hidrojen üretimi ölçümleri de gerçekleştirilmiştir.



Şekil 4. 1 PCA-ZnPc-2 sentez şeması

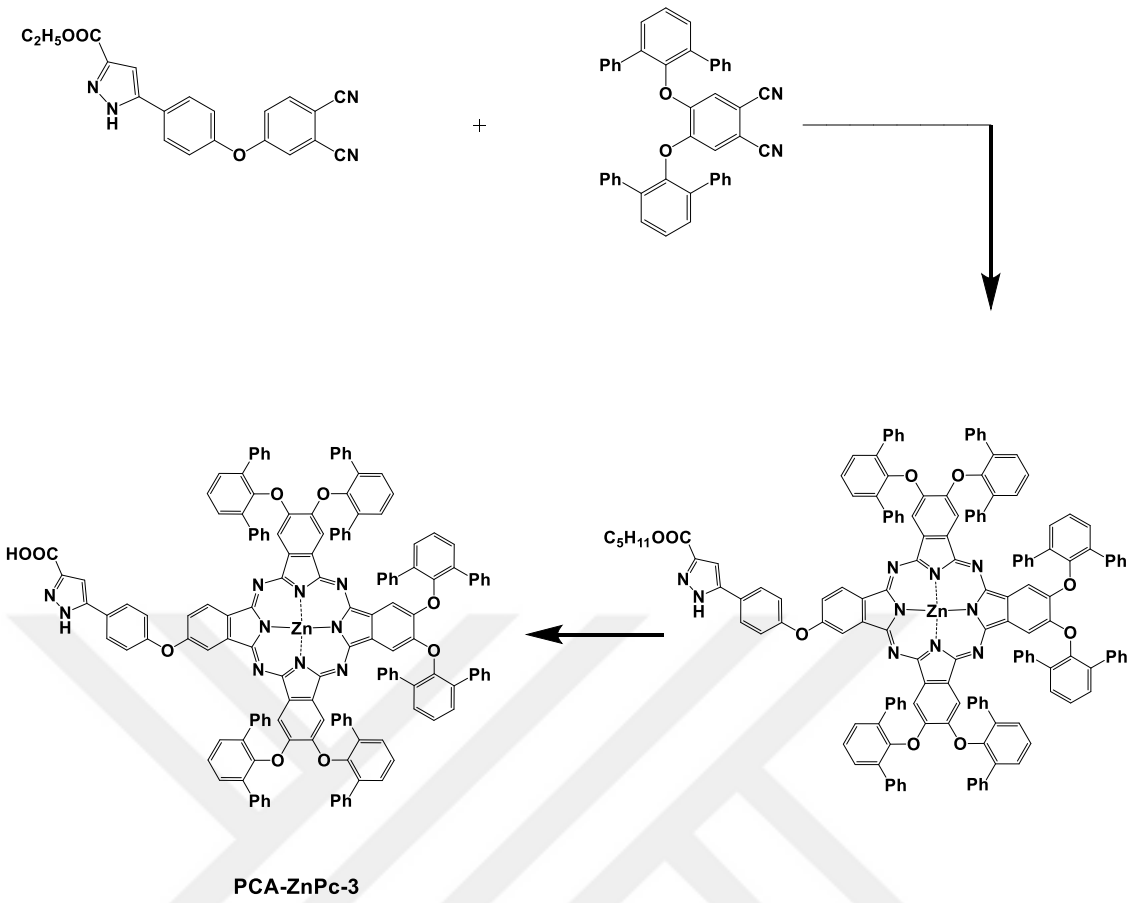
5

YARDIMCI ADSORBENT KULLANILMAYAN BOYA DUYARLI GÜNEŞ PİLLERİ İÇİN HACİMLİ DONÖR DİFENİL FENOKSİ GRUPLARI VE BAĞLAYICI PİRAZOL-3 KARBOKSİLİK ASİT İÇEREN AGREGE OLMAYAN ÇİNKO FTALOSİYANİN

Güneş Enerjisi, sayı 226, pp. 173–179, 2021.

Bu çalışmada agregasyon etkisini ve yardımcı adsorbent kullanımını tamamen ortadan kaldırarak bağlayıcı grup pirazol-3-karboksilik asit ihtiva eden asimetrik ftalosiyaninin maksimum güç dönüşüm verimliliğini tespit etmek amacıyla hacimli aromatik altı tane 2,6-difenil fenol grubu ve bir tane pirazol-3-karboksilik asit grubu içeren asimetrik çinko ftalosiyanin sentezlenmiştir. 4,5-bis(2,6-difenilfenoksi) ftalonitril bileşiği literatüre göre sentezlenmiştir [33]. Yukarıdaki ilk yayında sentez yöntemi belirtilen 5-[4-(3,4-disiyanofenoksi)-fenil]-1H-pirazol-3-karboksilik asit etil ester bileşiği tekrar elde edilmiştir. Bu iki ftalonitril türevinin $ZnCl_2$ ve DBU varlığında pentanol içerisindeki reaksiyonundan asimetrik çinko ftalosiyanin elde edilmiştir. Gerekli saflaştırma işlemleri yapılan bu bileşikte de yine etil ester yapısı pentil estere dönüşmüş olup, NaOH çözeltisi ve THF içerisinde hidroliz edilerek hedeflenen pirazol-3-karboksilik asit bağlayıcı grubu içeren asimetrik çinko ftalosiyanin sentezlenmiştir. Yeni bileşiklerin yapıları IR, Kütle, ^{1}H-NMR, ^{13}C-NMR, UV-Vis gibi spektroskopik yöntemlerle karakterize edilmiştir.

Elde edilen bileşiğin boya duyarlı güneş pili ölçümleri gerçekleştirilmiş ve yardımcı adsorbent kullanılmadan güç dönüşüm verimliliği % 1,97, yardımcı adsorbent kullanılarak ise güç dönüşüm verimliliği % 2,04 olarak tespit edilmiştir. Yardımcı adsorbent kullanımı güç dönüşüm verimliliği üzerinde hemen hemen hiç etki göstermemiştir.



Şekil 5. 1 PCA-ZnPc-3 sentez şeması

6
SONUÇ VE ÖNERİLER

Tez kapsamında ilk olarak boya duyarlı güneş pillerinde karboksilik asit bağlayıcı grubuna alternatif olabileceği düşünülen pirazol-3-karboksilik asit grubu içeren yeni asimetrik ftalosiyaninler başarılı bir şekilde sentezlenmiş ve yapıları karakterize edilerek tez kapsamında yayınlanan makalelerde sonuçlar ayrıntılı olarak verilmiştir.

Birinci makalemizde boya duyarlı güneş pili uygulaması sonucunda agregasyonu engelleyici yardımcı adsorbent kullanılmadan % 1,29, yardımcı adsorbent kullanılarak ise % 1,74'lük bir güç dönüşüm verimliliğine ulaşılmıştır. Literatürde daha önce bulunan ve bizim molekülümüzden **(PCA-ZnPc-1)** yapısal olarak tek farkı karboksilik asit bağlayıcı grubu içermesi olan **TT4** molekülü ile kıyaslama yapıldığında yaklaşık 3 kat daha fazla bir güç dönüşüm verimlliliği elde edildiği gözlemlenmiştir. Ayrıca literatürde genellikle TiO_2 kaplı iletken camın boyaya daldırılma süresi 24 saat iken, **PCA-ZnPc-1** molekülünde 2 saatlik daldırılma süresinde maksimum verime ulaşılmıştır. Diğer çalışmalarda pirazol-3-karboksilik asit bağlayıcı grubunun bu performasından sonra bağlayıcı grubu sabit tutup diğer grupları değiştirerek yeni asimetrik ftalosiyaninler sentezleyip güç dönüşüm verimliliğinin artırılması hedeflenmiştir.

Nitekim tez kapsamında yayınlanan ikinci makalede hem agregasyonu bir miktar daha azaltabilecek hem de daha fazla elektron verici gruplar içeren hekzil sülfanil sübstitüe ftalonitril bileşiği kullanılmasına karar verilmiştir. Başarılı bir şekilde sentezlenen bileşiğin boya duyarlı güneş pili uygulamalarında yardımcı adsorbent kullanılmadan % 1,67, yardımcı adsorbent kullanılarak % 1,89 güç dönüşüm verimliliği elde edilmiştir. Yardımcı adsorbent kullanılmadan bir önceki molekülümüz ile kıyaslandığında güç dönüşüm verimliliğinde yaklaşık % 30'luk bir artış olmuştur. Bunun yanı sıra yardımcı adsorbent kullanarak ve kullanmayarak elde edilen güç dönüşüm verimlilikleri kıyaslandığında ise **PCA-**

ZnPc-1 de bu oran yaklaşık % 35 iken, **PCA-ZnPc-2** de ise bu oran % 13'e kadar gerilemiştir. Bu sonuç agregasyon etkisinin azaltıldığını doğrulamaktadır.

Yardımcı adsorbent kullanımı agregasyonu azaltarak olumlu yönde katkıda bulunmasına rağmen boya üzerine adsorplanan boya miktarını azaltmaktadır. Bu amaçla literatürde yardımcı adsorbent kullanmayı gerektirmeyecek hacimli aromatik gruplar kullanılarak maksimum verimlere ulaşılmıştır. Tez kapsamındaki üçüncü makalede hacimli aromatik grup olarak 2,6-difenilfenol grubu taşıyan ftalonitril türevi kullanılmıştır. Sentezlenen bileşiğin boya duyarlı güneş pili ölçümleri yapılmıştır. Yardımcı adsorbent kullanılmadan güç dönüşüm verimliliği % 1,97 iken yardımcı adsorbent eklenmiş halinde ise % 2,04'tür. Değişim sadece % 3,5'tir. Bu da neredeyse agregasyonun hiç olmadığını kanıtlar niteliktedir. **PCA-ZnPc-3** molekülümüz yardımcı adsorbent kullanılmadan güç dönüşüm verimliliğinde **PCA-ZnPc-1**'e göre % 53, **PCA-ZnPc-2**'ye göre ise % 18'lik bir artış göstermiştir.

Tüm çalışmaların sonuçları başlangıçtaki beklentileri karşılamış olup, artık literatürde pirazol-3-karboksilik asidin boya duyarlı güneş pili uygulamalarında kullanılabilecek önemli bir bağlayıcı grup olabileceği kanıtlanmıştır.

Güç dönüşüm verimliliğinin, bağlayıcı grubun ftalosiyanin halkasına konjuge halde olduğu durumlarda 5 kata kadar artırılabildiğini gösteren yayınlar mevcuttur. Bu bilgiler ışığında pirazol-3-karboksilik asit bağlayıcı grubunu ftalosiyanin halkasına konjuge hale getirerek ftalosiyanin esaslı güneş pillerinde rekor güç dönüşüm verimliliklerine ulaşmak için çalışmalarımız devam etmektedir.

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A

PYRAZOLE-3-CARBOXYLIC ACID AS A NEW ANCHORING GROUP FOR PHTHALOCYANINE-SENSITIZED SOLAR CELLS

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Abstract

We have designed and synthesized an unsymmetrical zinc phthalocyanine (**PCA-ZnPc-1**) bearing an electron-withdrawing pyrazole-3-carboxylic acid anchoring group and three electron-donating *tert*-butyl groups as a sensitizer for dye-sensitized solar cells (DSSCs). **PCA-ZnPc-1** sensitized solar cell showed a modest power conversion efficieny (1.74%), which may suffer from the flexible and non-conjugated oxygen linker on the sensitizer. However, the obtained efficiency is found to be three to four times higher than that of the unsymmetrical ones bearing only carboxylic acid due to the combination of pyrazole and carboxylic acid moieties within the same anchoring group, which enhances the binding of the dye on the TiO_2 surface and results in an increase of electron injection efficiency. Therefore, the pyrazole-3-carboxylic acid is a promising anchoring group for developing new phthalocyanines to build efficient DSSCs.

Keywords: Dye-sensitized solar cells, Phthalocyanine, Anchoring group, Pyrazole-3-carboxylic acid.

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A.1 Introduction

Dye-sensitized solar cells (DSSCs) are an important solar energy conversion technology that have advantages include their ease and low cost of fabrication and tunable aesthetic features such as color and transparency [1], [2]. The main components of DSSCs are semiconducting metal oxide nanoparticles and dye molecules (sensitizer), which collectively act as working electrode of a DSSC, the redox mediator, the transparent conducting and counter conducting electrodes [3]. In recent years, a number of studies have been conducted to improve the performance of DSSCs by replacing the components with alternative ones [4]-[6]. The dye molecule, which is a fundamental component of the DSSCs, harvests solar photons and initiates charge separation through photoinduced electron transfer from the dye excited state into the conduction band of the metal oxide. The resulting oxidized dyes are subsequently reduced by the redox mediator [7]. Due to its high extinction coefficient in the red/near-infrared (NIR) region and chemical and thermal stability, phthalocyanine has been used as a dye in DSSCs [8]-[10]. In particular, many research groups have been focused on the field of phthalocyanine-sensitized solar cells after the studies on photovoltaic properties of ABBB-type unsymmetrical carboxylic acid substituted zinc phthalocyanines (**PCH001** and **TT1**) performed by Nazeeruddin et al. [10]-[12]. The common structural feature of these zinc phthalocyanine (ZnPc) dyes was that they were unsymmetrically substituted with three electron-donating *tert*-butyl groups (referred to as B) and one or more –COOH anchoring group (referred to as A). Nazeeruddin and coworkers were able to achieve power conversion efficiencies up to 4.1% by using ABBB-type ZnPcs sensitizers bearing *tert*-butyl donors and –COOH anchoring groups [13], [14]. Phthalocyanine dyes have a tendency to dissociate gradually from the metal oxide (TiO_2) surface, lose their capability to convert photons to electrons, and reduce the long-term stability of solar cells [15]. Therefore, immobilization of the adsorbing dye molecules onto the surface of TiO_2 nanoparticles is very important and usually achieved by addition of an “anchoring group”, i.e., a chemical substituent

able to adsorb the dye molecule onto the TiO_2 surface, resulting in efficient electron transfer from the dye into the TiO_2 conduction band [16], [17]. Although the most frequently used anchor in phthalocyanine-sensitized solar cells is carboxylic acid group, many new anchors have emerged and been tested [18]-[20]. Despite six major types of possible anchoring modes have been identified for carboxylic acid, the structures with bidentate modes (chelating and bridging) usually exhibit superior stability compared to others (Figure A.1a) [17].

Pyrazole-3-carboxylic acid possesses two N-donors on the pyrazole ring and two O-donors on the carboxylate and can show flexible coordination modes when coordinates with metal ions [21]-[23]. The N and O atoms of pyrazole-3-carboxylic acid can chelate to metal ions and form very stable complexes [24]. It is expected that such chelation can enforce the binding of phthalocyanine dyes onto the TiO_2 surface and decrease their dissociation from the surface, which results in the enhancement of electron injection efficiency and stability of the cell [14], [25]. Based on considerations above, we report for the first time that pyrazole-3-carboxylic acid is an alternative anchoring group to carboxylic acid in phthalocyanine dyes. To demonstrate its potential, unsymmetrical zinc phthalocyanine containing pyrazole-3-carboxylic acid (**PCA-ZnPc-1**) was synthesized and its optical, electrochemical and photovoltaic properties were investigated. Possible chelating and bridging modes of pyrazole-3-carboxylic acid substituted zinc phthalocyanine **PCA-ZnPc-1** are shown in Figure A.1b [20]. It was found that DSSC with **PCA-ZnPc-1** showed a promising power conversion efficiency of 1.74%, possibly due to its good adsorption affinity to the TiO_2 surface.

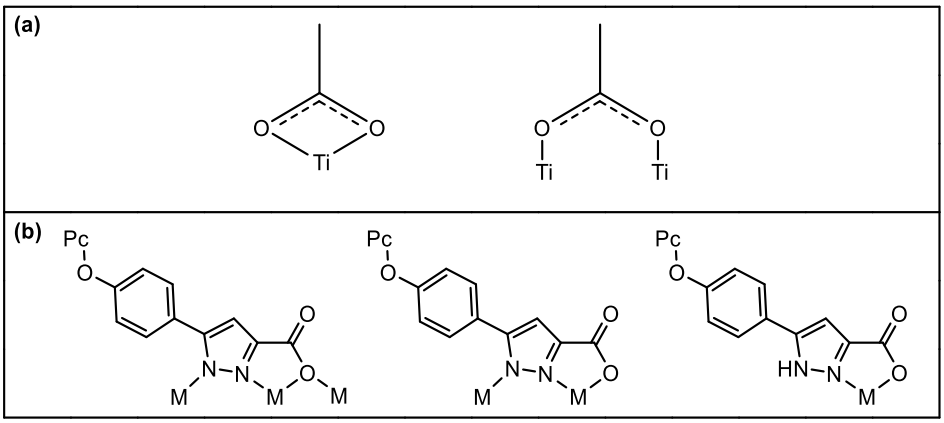


Figure A.1 Possible chelating and bridging modes of (a) Carboxylic acid and (b) **PCA-ZnPc-1**.

A.2 Experimental

A.2.1 Materials and methods

IR spectra were recorded on a Thermo Scientific iS10 FT-IR (ATR sampling accessory) spectrophotometer, and electronic spectra on a Shimadzu UV-2450 and 2600 UV-Vis spectrophotometer. ^{1}H and ^{13}C-NMR spectra were recorded on a Bruker Avance III 500 MHz spectrometer using TMS as an internal reference. Mass spectra were measured on an Agilent 6530 LC-MS/QTOF, Shimadzu Axima Performance and Bruker Microflex LT MALDI TOF-MS. Elemental analyses were performed on a Thermo FlashEA 1112. Melting points were determined on an Electrothermal Gallenkamp apparatus. All reagents and solvents were of reagent grade quality and were obtained from commercial suppliers. Special reagents 4-nitrophthalonitrile, 4-*tert*-butyl phthalonitrile and 3-(4-hydroxyphenyl)-1*H*-pyrazole-5-carboxylic acid were purchased from Sigma-Aldrich. 3-(4-hydroxyphenyl)-1*H*-pyrazole-5-carboxylic acid ethyl ester has been reported previously [26]. Here, this compound was synthesized using a Fischer esterification reaction as a different method than the literature.

Cyclic voltammetry (CV) and square wave voltammetry (SWV) were performed using a potentiostat/galvanostat (PARSTAT 2273, USA). The voltammograms were recorded in degassed 0.1 M tetrabutylammonium tetrafluoroborate/dimethyl sulfoxide (TBATFB/DMSO) solution containing

0.3 mM **PCA-ZnPc-1** in a three-electrode conic cell (working volume 10 mL). The cell equipped with glassy carbon working electrode (GCE, 3 mm diameter), Pt wire counter electrode and Pt disk as a pseudo-reference electrode. The working electrode potentials were calibrated using ferrocene/ferrocenium (Fc/Fc^+) redox couple solution as an external reference. Electrochemical impedance (EIS) measurements were recorded under dark at a forward bias of −0.55 V with AC amplitude of 10 mV at room temperature.

A double layer TiO_2 photoanode was prepared by previously reported procedures, [27], [28] as described below. An adhesive tape (Scotch™, 3M) with a window of 0.196 cm^2 area and 50 μm depth was applied to the conductive surface of the fluorine-doped tin oxide-coated glass electrode (FTO) (Solaronix, TCO22–15, 15 Ω cm^{-2}). A thin TiO_2 blocking layer was deposited onto FTO by dipping the tape-coated FTO in 40 mM aqueous solution of $TiCl_4$ for 30 min at 70 °C followed by rinsing with deionized water. Then, an anatase TiO_2 paste with an average particle size of ~ 20 nm (Solaronix Ti-Nanoxide T/SP) was coated on this electrode by the doctor blade method. The tape was removed and the TiO_2 electrode was gradually heated at 500 °C, followed by heating at the same temperature for 30 min in air. After cooling, the coating and heating processes were repeated over the previously coated electrode to obtain double layer TiO_2. The TiO_2 electrode was cooled to room temperature and again treated with the $TiCl_4$ solution, which was then heated at 500 °C for 30 min. After cooling to 80 °C, the resultant TiO_2 photoanode was sensitized with 0.1 mM **PCA-ZnPc-1** in a methanol solution for 2 h. 5 mM chenodeoxycholic acid (CDCA) as a co-adsorbent was also added into the dye solution to suppress the aggregation of dye. As a reference DSSC, the TiO_2 photoanode was also dipped in an ethanol solution containing 0.5 mM N719 (Solaronix, Ruthenizer 535-bisTBA) and 5 mM CDCA for 6 h. Pt-coated FTO was used as counter electrode. The sensitized TiO_2 photoanode and the counter electrode were assembled using a 25 μm–thick sealing spacer (Solaronix, Meltonix 1170−25) and an I^-/I_3^- electrolyte solution (Solaronix, Iodolyte HI−30).

The DSSC's photocurrent–voltage (*J–V*) characteristics were carried out using the above-mentioned potentiostat/galvanostat under a solar simulator (96000, Newport, USA) with AM 1.5G illumination (100 mW cm^{-2} = 1 sun). The measurement of incident photon to current conversion efficiency (IPCE) was recorded by using a monochromator (74004, Oriel, USA). The cells were covered with a black mask (0.196 cm^2) during the photovoltaic measurements.

A.2.2 Synthesis of 3-(4-hydroxyphenyl)-1H-pyrazole-5-carboxylic acid ethyl ester

To a solution of 3-(4-hydroxyphenyl)-1*H*-pyrazole-5-carboxylic acid (204 mg, 1 mmol) in 12 mL ethanol was added catalytic amount of conc. H_2SO_4 (2 drops) and refluxed under heating overnight. The reaction mixture was evaporated to remove solvent and then yellow-white precipitate was stirred in diethyl ether. Resultant white solid was filtered and dried under reduced pressure. Yield 229 mg (98.7%) M.p: 142-143 °C. FT-IR (ATR): ν_{max}, cm^{-1} 3387 (OH), 3284 (NH), 3053 (CH, aromatic), 2988-2943 (CH, aliphatic), 1745 (C=O).

A.2.3 Synthesis of 5-[4-(3,4-dicyanophenoxy)-phenyl]-1H-pyrazole-3-carboxylic acid [1]

4-nitrophthalonitrile (173 mg, 1 mmol) and 3-(4-hydroxyphenyl)-1*H*-pyrazole-5-carboxylic acid (408 mg, 2 mmol) were dissolved in 40 mL dry DMF. Anhydrous potassium carbonate (480 mg, 3.5 mmol) was added to the reaction solution in portions over 30 min. The reaction mixture was stirred at room temperature during 3d under argon atmosphere. The mixture was poured into ice-water (200 mL) and acidified to pH: 1 by diluted hydrochloric acid. The white precipitate was collected by filtration, thoroughly washed with water until the filtrate was neutral, dried under vacuum. Yield 260 mg (78.8%) M.p: 281-282 °C (decarboxylation). FT-IR (ATR): ν_{max}, cm^{-1} 3200-2500 (COOH), 3322 (NH), 3097-3034(CH, aromatic), 2237 (C≡N), 1689 (C=O). ^{1}H-NMR (DMSO-d_6): δ, ppm 13.57 (br, -NH, -COOH, 2H), 8.13-8.11 (d, Ar-H, 1H), 7.98-7.96 (d, Ar-H, 2H), 7.86-7.85 (d, Ar-H, 1H), 7.47-7.44 (dd, Ar-H, 1H), 7.28 (s, pyrazole-H, 1H),

7.26-7.27 (d, Ar-H, 2H). ^{13}C-NMR (DMSO-d_6): δ, ppm 160.84, 153.56, 136.28, 127.42, 126.67, 122.83, 122.19, 120.68, 116.70, 115.88, 115.55, 115.35, 108.31, 105.35. MS (HR LC/MS): *m/z* 353.0641 $[M+Na]^+$, 331.0823 $[M+H]^+$. Anal. calcd for $C_{18}H_{10}N_4O_3$: C, 65.45; H, 3.05; N, 16.96 (%). Found: C, 65.40; H, 2.99; N, 16.98 (%).

A.2.4 Synthesis of 5-[4-(3,4-dicyanophenoxy)-phenyl]-1H-pyrazole-3-carboxylic acid ethyl ester [2]

4-nitrophthalonitrile (113 mg, 0.658 mmol) and 5-(4-hydroxyphenyl)-2*H*-pyrazole-3-carboxylic acid ethyl ester (229 mg, 0.987 mmol) were dissolved in 25 mL dry DMF. Anhydrous potassium carbonate (120 mg, 0.875 mmol) was added to the reaction solution in portions over 2h. The reaction mixture was stirred at room temperature during 3d under argon atmosphere. The mixture was poured into ice-water (375 mL). The white precipitate was collected by filtration, dried under vacuum and recrystallized from ethanol. Yield 196 mg (83.2%) M.p: 230 ºC. FT-IR (ATR): ν_{max}, cm^{-1} 3237 (NH), 3108- 3068 (CH, aromatic), 2991-2899 (CH, aliphatic), 2231 (C≡N), 1708 (C=O). ^{1}H-NMR (DMSO-d_6): δ, ppm 14.04 (s, -NH, 1H), 8.12-8.10 (d, Ar-H, 1H), 7.96-7.92 (d, Ar-H, 2H), 7.85 (s, Ar-H, 1H), 7.45-7.44 (dd, Ar-H, 1H), 7.35 (s, pyrazole-H, 1H), 7.28-7.25 (d, Ar-H, 2H), 4.38-4.32 (m, -OCH_2, 2H), 1.32 (t, -CH_3, 3H). ^{13}C-NMR (DMSO-d_6): δ, ppm 160.67, 154.20, 142.43, 136.29, 127.49, 122.90, 122.37, 120.75, 116.70, 115.86, 115.34, 108.45, 105.44, 105.13, 55.99, 14.18. MS (HR LC/MS): *m/z* 739.2012 $[2M+Na]^+$, 359.1137 $[M+H]^+$. Anal. calcd for $C_{20}H_{14}N_4O_3$: C, 67.03; H, 3.94; N, 15.63 (%). Found: C, 67.01; H, 3.93; N, 15.65 (%).

A.2.5 Synthesis of 3

2 (50 mg, 0.140 mmol), 4-*tert*-butyl phthalonitrile (77.2 mg, 0.420 mmol), anhydrous $Zn(CH_3COO)_2$ (25.6 mg, 0.140 mmol) and 10 drops DBU were refluxed in n-pentanol (3 mL) for 24 h under an argon atmosphere. After cooling to room temperature, the reaction mixture was poured into n-hexane (30 mL) and the resulting precipitate was filtered off and washed with n-hexane. The green mixture of phthalocyanine was purified by silica

gel column chromatography. Symmetric 4-*tert*-butyl phthalocyanine was eluted using n-hexane:THF (4:1). Then asymmetric phthalocyanine **3** was eluted using n-hexane:THF (16:5). Yield: 17.4 mg (12.25%). FT-IR (ATR): ν_{max}, cm^{-1} 3065 (CH, aromatic), 2954-2869 (CH, aliphatic), 1719 (C=O). ^{1}H-NMR ($CDCl_3$): δ, ppm 9.03-6.42 (br, Ar-H), 4.55-4.18 (br, -OCH_2), 1.54-0.80 (m, aliphatic -CH_2 and -CH_3). MS (MALDI TOF): *m/z* 1016.928 $[M+H]^+$. UV-Vis (THF, 1.0 $\times 10^{-5}$ M): λ_{max}, nm (log ε) 672 (5.17), 607 (4.38), 349 (4.70). Anal. calcd for $C_{59}H_{56}N_{10}O_3Zn$: C, 69.57; H, 5.54; N, 13.75 (%). Found: C, 69.51; H, 5.49; N, 13.81 (%).

A.2.6 Synthesis of PCA-ZnPc-1

To a solution of **3** (52.9 mg, 0.052 mmol) in THF was added 1 M NaOH (2 mL). The mixture was stirred at 60 °C for 48 h and monitored by TLC (n-hexane:THF (16:5)). After completion, the reaction mixture was cooled to room temperature and evaporated to dryness under reduced pressure. Then water was added and the residue was acidified to pH: 2 by diluted HCl. The blue precipitate was centrifuged, washed with water and n-hexane. The blue solid was dried under vacuum. Yield: 25.5 mg (51.8%). FT-IR (ATR): ν_{max}, cm^{-1} 3498-2500 (COOH), 3183 (NH), 3077 (CH, aromatic), 2954-2864 (CH, aliphatic), 1661 (C=O). ^{1}H-NMR ($CDCl_3$): δ, ppm 9.39-6.43 (br, Ar-H), 1.69-1.18 (m, aliphatic-H). MS (MALDI TOF): *m/z* 947.9226 $[M]^+$. UV-Vis (THF, 1.0 $\times 10^{-5}$ M): λ_{max}, nm (log ε) 674 (5.26), 608 (4.52), 349 (4.82). Anal. calcd for $C_{54}H_{46}N_{10}O_3Zn$: C, 68.39; H, 4.89; N, 14.77 (%). Found: C, 68.21; H, 4.86; N, 14.79 (%).

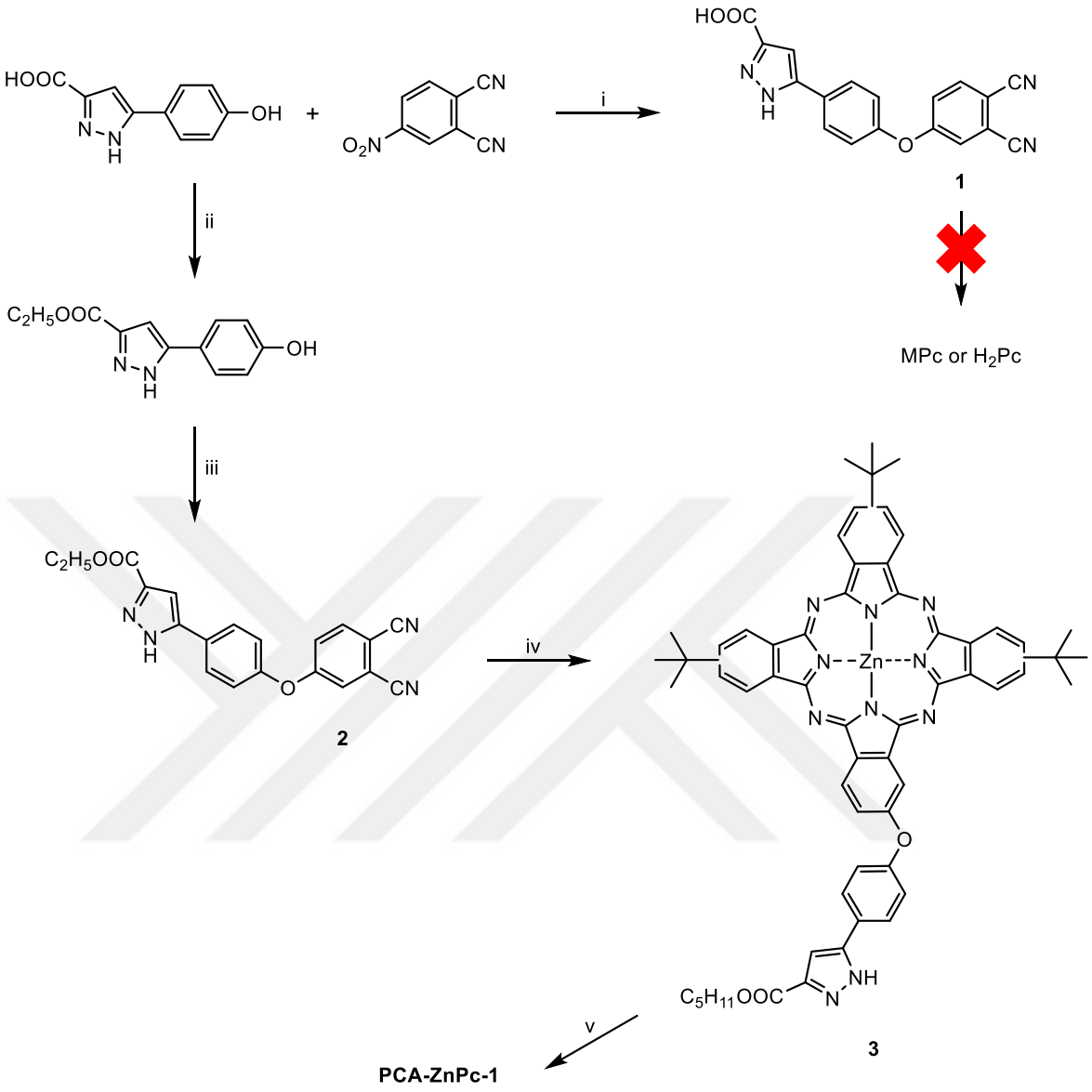
A.3 Results and Discussion

A.3.1 Syntheses

In this study, new ABBB-type unsymmetrical pyrazole-3-carboxylic acid substituted zinc phthalocyanine **PCA-ZnPc-1** was synthesized using statistical condensation method (or mixed cyclotetramerization). The statistical condensation method is the oldest and most popular synthetic method for the preparation of the ABBB-type unsymmetrical

phthalocyanines [29]. It is based on the statistical reaction of two differently substituted phthalonitriles, affording in principle a mixture of six compounds. Therefore, chromatographic separation is usually required to isolate the desired ABBB-type macrocycle from the mixture [30]. One of the phthalonitriles is usually employed in excess, typically in a 3:1 molar ratio, thus favoring the formation of the ABBB-type phthalocyanine. Under this reaction condition, the theoretical yields of products are as follows: AAAA (33%), ABBB (44%), and other condensation products (23%) [31]. Scheme 1 shows the synthetic route to **PCA-ZnPc-1**. At first, we tried to synthesize **PCA-ZnPc-1** directly by mixed cyclotetramerization of pyrazole-3-carboxylic substituted phthalonitrile and 4-*tert*-butyl phthalonitrile. For this purpose, phthalonitrile derivative **1** was obtained using conventional method based on aromatic nucleophilic substitution. However, despite all our attempts, we could not isolate our target molecule **PCA-ZnPc-1** from the mixed cyclotetramerization reaction of **1** and 4-*tert*-butyl phthalonitrile. Upon this, 3-(4-hydroxyphenyl)-1*H*-pyrazole-5-carboxylic acid was converted to its ester derivative named 3-(4-hydroxyphenyl)-1*H*-pyrazole-5-carboxylic acid ethyl ester by Fischer esterification method. Here, the ester group was used as a "protecting group" necessary for a successful separation of the phthalocyanine mixtures. In the next step, 3-(4-hydroxyphenyl)-1*H*-pyrazole-5-carboxylic acid ethyl ester was reacted with 4-nitrophthalonitrile to give phthalonitrile derivative **2** in 83.2% yield.

Heating the phthalonitrile **2** in n-pentanol with zinc(II) acetate and catalytic amount of DBU led to the phthalocyanine system **3** as a statistical mixture. Under these conditions, a transesterification of the ethyl ester functions to the corresponding pentyl ester **3** was observed [32], [33]. After chromatographic purification and characterization, the ester phthalocyanine **3** is hydrolyzed to the carboxylic acid **PCA-ZnPc-1**. The hydrolysis of the ester group was realized by heating in the mixture of 1 M NaOH and THF. After the hydrolysis, the product was acidified, washed with water and n-hexane and dried under vacuum.



Scheme A.1 Synthesis of **PCA-ZnPc-1**. (i) K_2CO_3, DMF, 3 d; (ii) C_2H_5OH, H_2SO_4, reflux, overnight; (iii) 4-nitrophthalonitrile, K_2CO_3, DMF, 3 d; (iv) 4-*tert*-butyl phthalonitrile, $Zn(CH_3COO)_2$, DBU, n-pentanol, 24 h; (v) 1 M NaOH, THF, 60 °C, 48 h.

A.3.2 Structural characterizations

All of the new compounds were fully characterized with various spectroscopic techniques such as FT-IR, MS, ^{1}H-NMR, ^{13}C-NMR, UV-Vis, and X-ray crystallography. In the FT-IR spectra of phthalonitrile derivatives **1** and **2**, stretching vibrations of N-H (3322 $cm^{-1}$and 3237 cm^{-1}), C≡N (2237 cm^{-1} and 2231 cm^{-1}), C=O (1689 cm^{-1} and 1708 cm^{-1}), and aromatic C-H

(3108-3034 cm^{-1}) appeared at expected frequencies. As a difference, stretching vibrations of O-H at 3200-2500 cm^{-1} were observed for **1**, while the aliphatic C-H stretching vibrations at 2991-2899 cm^{-1} were observed for **2** in the FT-IR spectra. The IR spectrum of **2** and **3** were similar, the only difference being the disappearance of the C≡N vibration in the latter compound. In the FT-IR spectrum of **PCA-ZnPc-1**, the presence of characteristic broad stretching vibration of carboxylic acid O-H and shifting of C=O peak from 1719 cm^{-1} to 1661 cm^{-1} indicated that hydrolysis had taken place.

In the mass spectra of phthalonitrile derivatives (**1** and **2**), the $[M+H]^+$ peaks were observed at *m/z* 331.0823 and 359.1137 amu, respectively (Fig. S1). MALDI-TOF MS spectrum is very important for verifying of the structure in unsymmetrical phthalocyanines. In the MALDI-TOF MS spectrum, we only observed the molecular ion peak at *m/z* 1016.928 for **3** (Fig. S2). After hydrolysis of the ester group of the zinc phthalocyanine **3**, this peak was disappeared and the molecular ion peak of hydrolysis product **PCA-ZnPc-1** was appeared at *m/z* 947.9226 amu (Fig. S3). NMR investigations of **1** and **2** provided the characteristic chemical shifts for the structures expected (see experimental section). The ^{1}H-NMR spectra of unsymmetrical ZnPcs are somewhat broader than the corresponding signals in the phthalonitrile derivatives **1** and **2**. Tetrasubstituted phthalocyanines obtained from 4 substituted phthalonitriles are naturally a mixture of isomers which is a primary reason for the broadness of the peaks. In addition, the presence of the tautomeric forms of aryl-pyrazole-carboxylic acid can be considered as another reason for the broadness of the peaks in ^{1}H-NMR [34]. We couldn't observe heteroatom-bound protons in the ^{1}H-NMR spectrum of **PCA-ZnPc-1** as in the literature [35]-[38]. The main difference between the ^{1}H-NMR spectra of **3** and **PCA-ZnPc-1** is the absence of δ= 4.55-4.18 signal belonging to the ester group in the ^{1}H-NMR spectrum of **PCA-ZnPc-1**.

One of the best proofs for the formation of phthalocyanines and their metal complexes are supplied *via* their ground state electronic spectra in studied

solution. The electronic absorption spectrum of metallated phthalocyanine shows two characteristic bands: the Soret band near 340 nm and a single Q band between 600 and 800 nm due to a π-π^* ligand transition. These two bands are dependent on the electronic interactions between the ligand as well as by the state of the central atom and peripheral substitution [39], [40]. UV-Vis absorption spectra was recorded for the unsymmetrical phthalocyanines (**3** and **PCA-ZnPc-1**) in THF. Compound **3** and **PCA-ZnPc-1** showed the single Q band and same Soret band. Soret band values of **3** and **PCA-ZnPc-1** are 349 nm. The Q band values of zinc phthalocyanines **3** and **PCA-ZnPc-1** are 672 nm and 673 nm, respectively (Figure A.2).

The structure of **2** was also confirmed by X-ray analysis (Table S1). The ORTEP representation of the compound is shown in Figure A.3.

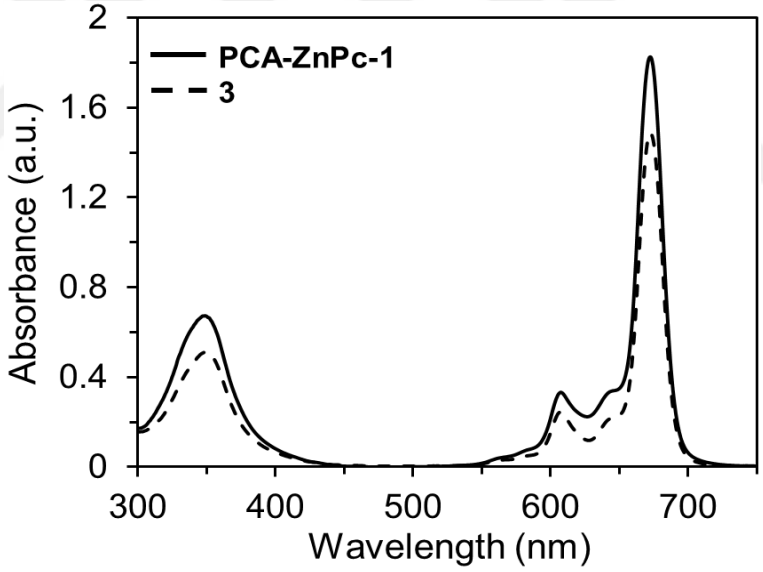


Figure A.2 UV-Vis absorption spectra of **3** and **PCA-ZnPc-1** in THF.

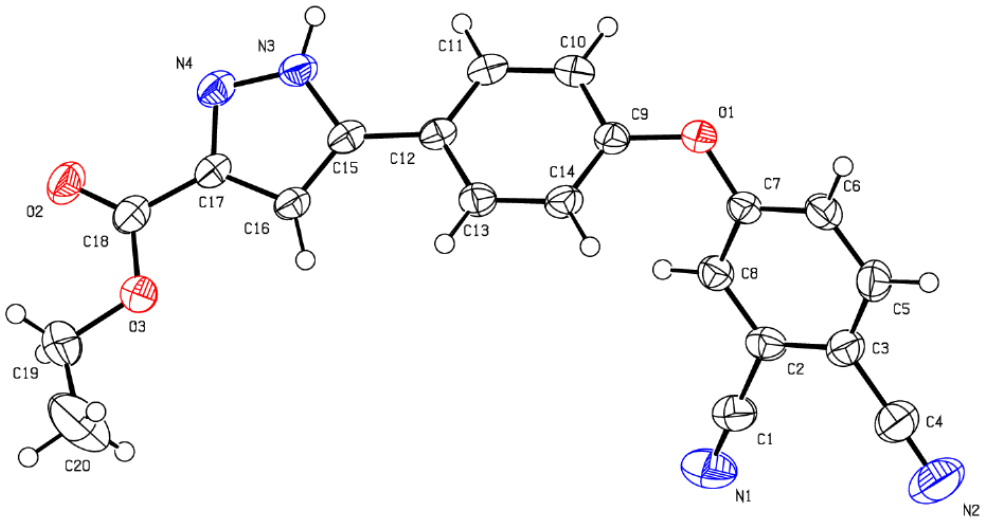


Figure A.3 The molecular structure of phthalonitrile **2**.

A.3.3 Electrochemical studies

To evaluate the redox stability and the molecular orbital energy levels, the electrochemical properties of **PCA-ZnPc-1** were investigated through CV and SWV, as shown in Fig. S4. Cyclic voltammogram of **PCA-ZnPc-1** exhibits one reversible reduction labeled as R_1 ($E_{1/2}$ = − 0.91 V) and one quasi-reversible oxidation labeled as O_1 ($E_{1/2}$ = 0.93 V) with respect to anodic to cathodic peak separations (ΔE_p) of 81 and 112 mV, respectively, at a scan rate of 100 mV s^{-1} (ΔE_p value for the reversible Fc/Fc^+ was 96 mV with the same scan rate) (Fig. S4a). The reversibility of the oxidative process remains almost unchanged at different scan rates, indicating that the dye shows good redox stability [41]. On the other hand, the peak currents of R_1 and O_1 processes increased linearly with the square root of the scan rate, suggesting their diffusion-controlled nature. These redox processes also confirmed by SWV, which is more sensitive than CV, as shown in Fig. S4b. The ground and excited state oxidation potentials (E_{ox} and E_{ox}*) vs. normal hydrogen electrode (NHE), correspond to the HOMO and the LUMO energy levels vs. vacuum, respectively, are summarized in Table 1. In a DSSC, for efficient electron injection and fast regeneration of oxidized dye, the E_{ox}* of dye should be higher than conduction band (CB) of TiO_2 while the E_{ox} of dye should be lower than electrolyte redox potential, both by at least 0.2 V [42], [43]. The E_{ox}* of **PCA-ZnPc-1** is lifted by 0.07 V with respect to CB of TiO_2

(– 0.5 V vs. NHE) and electron injection may be limited or slow [44]. However, the E_{ox} level is more positive than the electrolyte solution potential (0.4 V vs. NHE), suggesting that there is a sufficient driving force for dye regeneration.

Table A.1 Optical and electrochemical properties of **PCA-ZnPc-1**.

Dye	λ_{em} (nm[a]	λ_{max} (nm[b]	ε (10^5 mol^{-1} cm^{-1})[c]	λ_{onset} (nm)[d]	E_{0-0} (eV)[e]	$E_{1/2}$ (V)[f]	E_{ox} (V[g]	E_{ox}* (V)[h]	$E_{HOMO/LUO}$ (eV)[i]
PCA-ZnPc-1	678	674	1.82	693	1.79	0.59	1.22	–0.57	–5.39/–3.60

[a] Emission maxima was obtained in THF by excitation at 607 nm.

[b] Absorption maximum wavelength (λ_{max}) of the dye solution.

[c] Molar extinction coefficient (ε) of the dye.

[d] Absorption onset wavelength (λ_{onset}) of the dye solution.

[e] Band gap (E_{0-0}) was calculated from the absorption onset wavelength (λ_{onset}) using $E_{0-0} = 1240/\lambda_{onset}$.

[f] Redox potential ($E_{1/2}$) of O_1 was referred to the external Fc/Fc^+ standard (0.34 V vs. Pt disk pseudo-reference electrode). Therefore, the $E_{1/2}$ of O_1 can be converted to Fc/Fc^+ by subtracting 0.34 V.

A.3.4 Photovoltaic performance of DSSCs

Figure A.4a presents the *J-V* curves of **PCA-ZnPc-1** based DSSCs fabricated in methanol solvent without and with 5 mM of CDCA and their photovoltaic parameters are shown in Table 2. Firstly, without CDCA, the photovoltaic performance was optimized in terms of immersion time and dye surface density, as shown in Figure A.4b. The surface density (Γ) of the adsorbed dye on the TiO_2 film was estimated by measuring the difference in absorbances of the dye solution before and after immersion of the film [45]. Obviously, the dye reached almost saturated surface coverage on the film after 4 h immersion time. However, a highest power conversion efficiency

(PCE) of 1.29% was obtained at 2 h and then decreased slowly up to 12 h, indicating an increase in dye aggregation with increasing immersion time [46]. As shown in Fig. S5, with an increase in the immersion time, the color of the adsorbed dye changed from pale to dark also confirms the increase of dye loading. To further optimize the photovoltaic performance, **PCA-ZnPc-1** based DSSC sensitized in a different solvent, tetrahydrofuran (THF). However, the use of THF showed lower PCE (0.92%) and surface density (2.6×10^{-8} mol cm^{-2}) compared to the device sensitized in methanol. This lower PCE can be attributed to aprotic solvent property of THF which solvates the dye better, resulting in the lower surface density (Wu et al., 2012). Figure A.4a also shows the *J-V* curve of the DSSC sensitized in the presence of 5 mM CDCA as a co-adsorbent which is known to enhance device efficiency by disrupting the dye aggregation. This device exhibited short-circuit current (J_{SC}), open-circuit voltage (V_{OC}) and fill factor (FF) of 3.74 mA cm^{-2}, 0.628 V and 0.74, respectively, yielding an overall PCE of 1.74% which represents *ca.* 35% of improvement compared to the cell without CDCA. This result confirms the addition of CDCA into the dye solution certainly diminishes the aggregation of the dye. Finally, to optimize the cell performance, the dye was also sensitized in 2.5 and 7.5 mM CDCA. However, in the presence of former co-adsorbent, the DSSC showed lower performance (1.38%) than the cell with 5 mM CDCA, indicating the amount of CDCA partly prevents aggregation of the dye on the TiO_2. On the other hand, when 7.5 mM CDCA was used, the device performance decreased to 1.56% due to some of the adsorbed dye molecules replaced by CDCA [47]. Therefore, the optimum concentration of CDCA is determined as 5 mM.

Table A.2 Photovoltaic parameters of the DSSCs after 2 h immersion time.

Dye	IPCE integrated current density (mA cm^{-2})	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	PCE (%)
PCA-ZnPc-1	3.21	3.18	0.605	0.67	1.29
PCA-ZnPc-1 + CDCA	3.72	3.74	0.628	0.74	1.74
N719		15.18	0.821	0.64	7.98

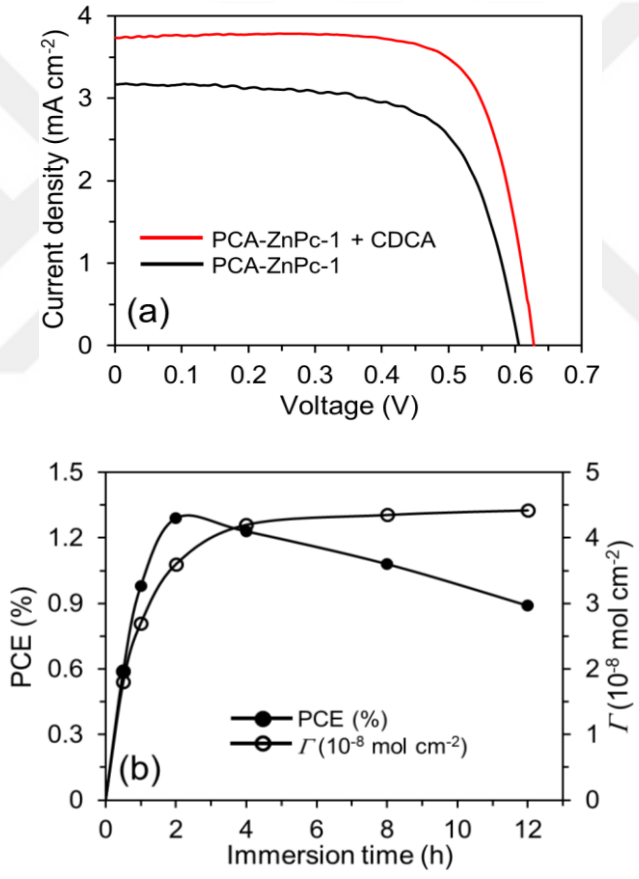


Figure A.4 (a) *J-V* curves of DSSCs based on **PCA-ZnPc-1** with and without CDCA. (b) Immersion time dependent curves of efficiency (PCE) and dye surface density (*Γ*) of **PCA-ZnPc-1** without CDCA.

It should be noted that the photovoltaic performance of **PCA-ZnPc-1** is lower than previously reported efficiencies of similar unsymmetrical phthalocyanines, namely **TT1**, **TT3** and **TT5**, containing *tert*-butyl groups,

conducting spacer and carboxylic acid [48]. Evidently, the low performance of **PCA-ZnPc-1** is probably caused by poor electronic conduction between the phthalocyanine core and the carboxylic acid due to flexible and non-conjugated oxygen linker [48], [49]. However, **PCA-ZnPc-1** has almost three to four times higher PCE with respect to **TT2** and **TT4** bearing *tert*-butyl groups, oxygen linker and carboxylic acid (Figure A.5) [48]. This can be attributed to the enhanced electron injection efficiency from the dye to the TiO_2 having better anchoring ability of the pyrazole-3-carboxylic acid moiety than carboxylic acid function alone [24]. The immersion time for **PCA-ZnPc-1** was found to be shorter than its counterparts (**TT1**-**TT5**) also indicates a stronger adsorption ability of the anchoring group. Furthermore, electron-withdrawing nitrogen atom on the pyrazole moiety may also enhance the photovoltaic performance [20].

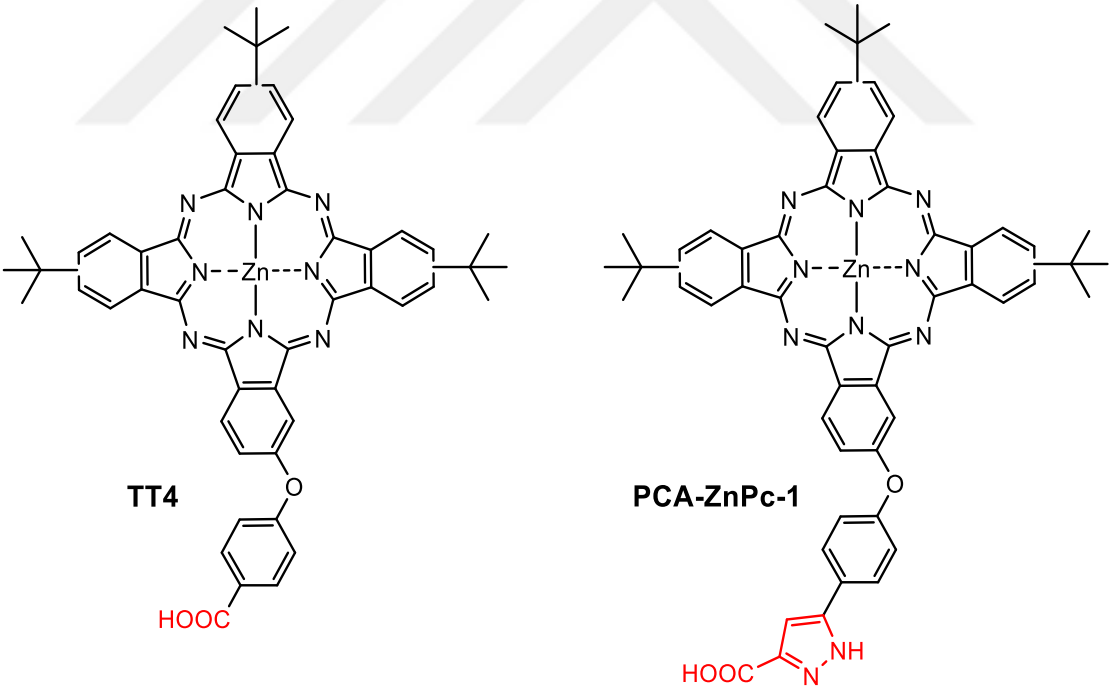


Figure A.5 Molecular structures of **TT4** [48] and **PCA-ZnPc-1**.

Aggregation of **PCA-ZnPc-1** was investigated by comparing absorption spectra of the adsorbed dye on the TiO_2 surface in the presence and absence of CDCA, as shown in Figure A.6a. Without CDCA, the Q band, corresponding to monomeric absorption, exhibited a red shift about 10 nm

compared to the solution absorption spectrum due to interaction of the anchoring group with the TiO_2 surface [12]. Furthermore, in contrast to the solution absorption spectrum, the adsorbed dye showed a new band at around 635 nm which is the characteristic Q-band of **PCA-ZnPc-1** face-to-face dimer or higher order aggregate [50]. Therefore, the dye is confirmed to exist as a mixture of monomer and aggregate on the TiO_2 surface. In the presence of CDCA, the absorption wavelengths of the Q and the aggregation bands did not change, but the ratio of the intensity of the aggregation band relative to the Q band decreased from 0.93 to 0.25 due to the competitive adsorption of the co-adsorbent. The effect of CDCA was also confirmed by IPCE recorded for DSSCs (Figure A.6b). Evidently, the maximum IPCE value increased from 32% to 44% in the presence of CDCA, suggesting the monomer can inject electrons to the surface more efficiently than the aggregate. The integrated J_{SC} values obtained from the IPCE spectra are in agreement with the results of the J–V experiment, confirming that the photovoltaic results are reliable (Table 2).

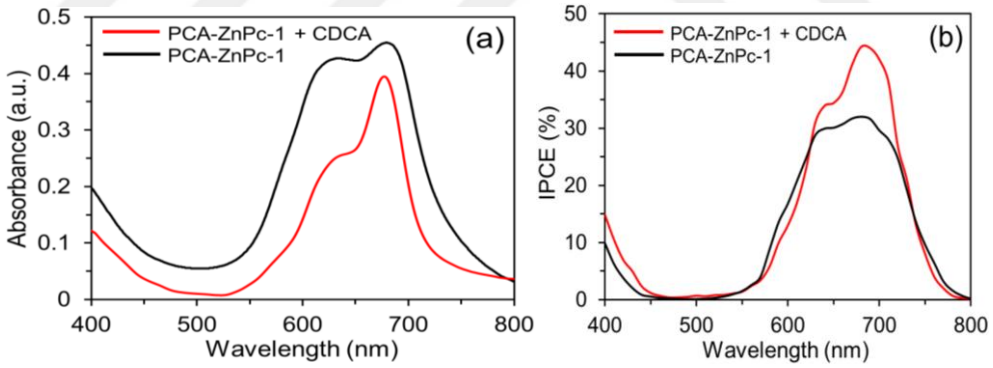


Figure A.6 (a) UV–vis absorption spectra of **PCA-ZnPc-1** with or without CDCA on TiO_2 film and (b) corresponding IPCE spectra.

To obtain information about the charge transfer process in the DSSCs, EIS was performed in the dark. The Nyquist plots in Figure A.7a showed two semicircles at low and high impedances, which are assigned to the charge transfer at the Pt/electrolyte and the TiO_2/dye/electrolyte, respectively [23]. As can be seen that the radius of the semicircle at high impedances for the DSSC with CDCA is larger than the device without CDCA. On the other hand, as shown in Bode plots (Figure A.7b), the low frequency peak of the

DSSC based on CDCA shifted to lower frequency relative to the device fabricated without CDCA, indicating a longer electron lifetime for the former. The longer electron lifetime indicates improved suppression of charge recombination process, thus resulting in higher V_{OC} [51]. The co-adsorbent effectively suppresses the recombination process by the more compact monolayer than does the adsorption of the dye alone, results in an increase in V_{OC}. In addition, the co-adsorbent acts to shift the CB of TiO_2 to more negative energy levels, also leading an increase of V_{OC} [52].

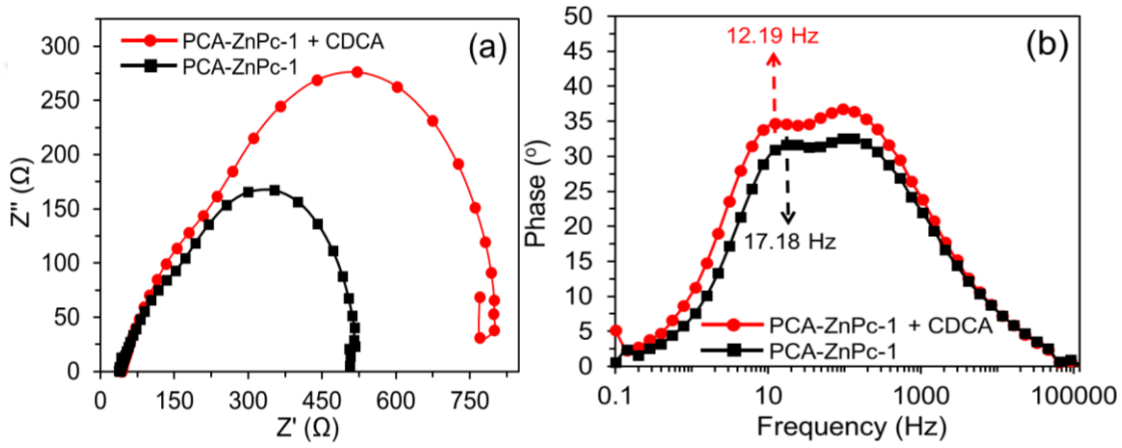


Figure A.7 (a) Nyquist and (b) Bode plots of DSSCs based on **PCA-ZnPc-1** with or without CDCA. The dashed arrows in panel (b) show the frequency maxima at the TiO_2/dye/electrolyte.

A.3.5 Theoretical calculations

All optimizations were carried out by Gaussian Software 09 in gas phase [54]. DFT calculations were performed using the B3LYP hybrid exchange-correlation functional and the 6-311G(d,p) basis set [53]. The geometry optimization was followed by frequency calculations, and no imaginary frequencies were found. Analysing of optimized structure of **PCA-ZnPc-1** revealed that phthalocyanine skeleton is planar and phenoxy unit showed deviation from planarity with 120.66 ° which is confirmed by X-ray analysis of **2** in which corresponding angle was found as 119.64 ° (Figure A.8).

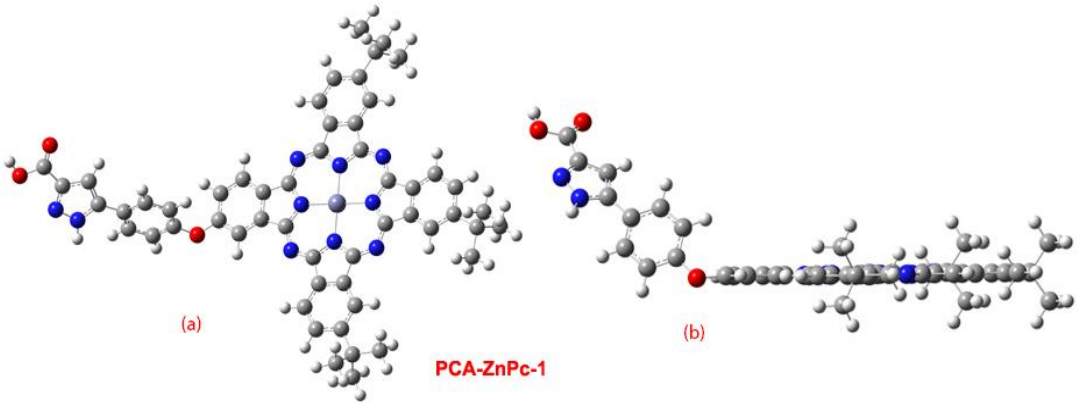


Figure A.8 Optimized structure of **PCA-ZnPc-1**: in front view (a) and side view (b).

To understand the reactivity of molecules, theoretical calculation and plotting of frontier molecular orbitals, HOMO (High Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital), were calculated using same hybrid method. These frontier orbitals are very important quantum parameters which play a role in the electrical and optical properties. HOMO and LUMO of **PCA-ZnPc-1** were plotted and their energies were calculated in eV (Figure A.9). HOMO and LUMO of **PCA-ZnPc-1** were localized on the phthalocyanine skeleton with small differences. Although HOMO is consist of all ZnPc skeleton, LUMO was localized on ZnPc unit except for that two phenyl rings of ZnPc, perpendicular to the phenoxy-pyrazole unit, did not noteworthy contribution on LUMO. However, phenoxy-pyrazole-carboxylic acid unit did not give any contribution on both HOMO and LUMO. Furthermore, energy gap of **PCA-ZnPc-1** was calculated as 2.168 eV which is close to experimental energy gap.

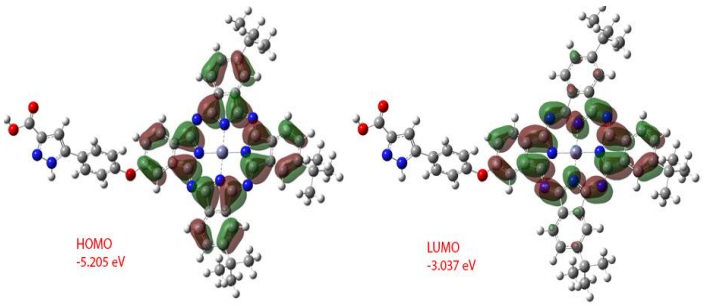


Figure A.9 HOMO and LUMO for **PCA-ZnPc-1**.

Pyrazole ring of phthalocyanine skeleton might possess two different tautomers. Although there are more than two tautomers for the pyrazole ring, the tautomers that disrupt the aromaticity over the carbon atom were neglected. Hydrogen atom attached to the nitrogen atom in one of tautomers is away from oxygen atom of carboxylic acid while hydrogen atom attached to nitrogen atom in the other is close to the oxygen atom of carboxylic acid. Hydrogen and oxygen atoms can therefore occur an intramolecular hydrogen bond resulting in decreasing energy. The free energies of two tautomers were calculated and it was seen that tautomer 2 of **PCA-ZnPc-1** is more stable than tautomer 1 about 2.52 kcal/mol (Fig. S6). Intramolecular hydrogen bonding might be responsible for decreasing the energy. Distance between hydrogen and oxygen atoms was found to be 2.51 Aº which is acceptable for hydrogen bonding [55]. Furthermore, forming of tautomer 2 revealed planar structure between pyrazole and adjacent phenyl ring. Hydrogen atom attached to the nitrogen atom of the pyrazole ring and hydrogen atom at ortho-position of the phenyl ring in tautomer 1 might occur repulsion. With this repulsion, both energy of tautomer 1 increases and deviation from planarity between two rings occurs. Dihedral angle between pyrazole and phenyl rings was found to be 30.5 º for tautomer 1 and 0.46 º for tautomer 2 which indicates that tautomer 1 showed more deviation from planarity between pyrazole and phenyl ring than that of tautomer 2 (Fig. S6). It was assumed that these effects might be responsible for the stability of tautomer 2.

A.4 Conclusions

In summary, a new unsymmetrical zinc phthalocyanine, **PCA-ZnPc-1**, bearing *tert*-butyl donor groups and a pyrazole-3-carboxylic acid anchoring group has been synthesized and characterized. The optical, electrochemical and theoretical studies suggested that the complex is suitable as a sensitizer in DSSCs. When tested in DSSC, the optimized **PCA-ZnPc-1** showed 1.74% power conversion efficiency with an IPCE value of 44% at 680 nm. The photovoltaic performance is considerably higher than that of the similar phthalocyanines containing only carboxylic acid. This might be attributed to

the stronger binding ability of the pyrazole-3-carboxylic acid with electron-withdrawing nitrogen atom, which leads to the improved electron injection efficiency. Overall, these results demonstrate that the unsymmetrical zinc phthalocyanine having pyrazole-3-carboxylic acid anchoring group is a promising sensitizer to harvest the red/near-IR regions.

Acknowledgements

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Appendix A. Supplementary Material

Supplementary data associated with this article can be found, in the online version at https://doi.org/10.1016/j.solener.2018.09.039.

A.5 References

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B

UNSYMMETRICALLY PYRAZOLE-3-CARBOXYLIC ACID SUBSTITUTED PHTHALOCYANINE-BASED PHOTOANODES FOR USE IN WATER SPLITTING PHOTOELECTROCHEMICAL AND DYE-SENSITIZED SOLAR CELLS

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Abstract

A new photosensitizer, **PCA-ZnPc-2**, was synthesized through the asymmetric functionalization of phthalocyanine ring with a pyrazole-3-carboxylic acid as the electron-withdrawing and anchoring group and six hexylsulfanyl as the bulky electron-donating groups. **PCA-ZnPc-2** was tested in dye-sensitized solar cells (DSSCs) and its performance was compared with **PCA-ZnPc-1**. It was found that **PCA-ZnPc-2** has higher electron-donating ability which is favorable for light harvesting and suppress the dye aggregation on TiO_2 when compared to **PCA-ZnPc-1**. Also, the new photosensitizer was used in dye-sensitized photoelectrochemical cells for hydrogen production under visible irradiation. The results show that **PCA-ZnPc-2** is a promising photosensitizer to harvest the red/near-IR regions.

Keywords: Phthalocyanine, pyrazole-3-carboxylic acid, dye-sensitized solar cells, photoelectrochemical hydrogen production

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B.1 Introduction

The chemistry of metallophthalocyanines (MPcs) is one of the most important topics for both fundamental and applied sciences [1]. There are many applications of MPcs such as chemical sensors [2], [3], liquid crystals [4] electrochromic materials [5], [6], photosensitizers (for photodynamic therapy) [7]-[9], and catalysts [10] in addition to the use as dyes and pigments. Since the syntheses of MPcs generally follow the classical cyclotetramerization of suitably substituted phthalonitriles, more synthetic efforts have focused on the preparation of substituted phthalonitriles with different functional groups. The addition of new properties to MPcs by the substitution of phthalonitriles results in new materials with the necessary functions for various application areas [11].

Zinc(II) phthalocyanines (ZnPcs) have been used as a dye in DSSC applications due to both their diamagnetic properties and long-lived (>1 ns) singlet excited states [12]-[14]. On the other hand, ZnPc dyes may show the poor photovoltaic performances chiefly owing to strong aggregation on the TiO_2 surface resulting in rapid deactivation of the dyes' excited states [15]. Aggregation can be prevented by substituting bulky aliphatic and aromatic groups that inhibit sterically intermolecular interaction [16]. Furthermore, the incorporation of bulky groups achieves a directional excited state to ease of electron injection onto TiO_2. The usage of bulky aliphatic electron-donating groups on Pcs not only prevents the intermolecular interaction but also arranges the LUMO level [11], [17], [18]. Besides the photovoltaic performance of DSSC, the long term stability of the device is another important issue that needs to be drilled. ZnPcs are substituted with "anchoring groups" to achieve a stable attachment of the dye onto the surface of metal oxide [19]. Historically, the most frequently used anchor in ZnPc based DSSCs is carboxylic acid which is generally able to attach onto a TiO_2 electrode through the interaction between the carboxylate and the titanium atoms present on the TiO_2 surface [20].

Photoelectrochemical (PEC) water splitting is one of the most reasonable approaches for hydrogen production to resolve energy problems of the future. Titanium dioxide (TiO_2) as semiconductor was first used for generation of

hydrogen from PEC water splitting by Honda and Fujishima in 1972 [21], and then increasing research has been performed to obtain electrodes using various semiconductor material. To achieve efficient splitting of water, the semiconductor photoanode should meet some properties, such as photochemically stable, suitable band position, strong absorption in the solar spectrum, low density of defects for efficient charge transfer, reduction of the electron-hole recombination, and low cost [22]-[24]. TiO_2 has superior features in comparison with metal oxides such as appropriate band gap structure, superior chemical, and optical stability and low cost [25]-[26]. Therefore, it is important for PEC water splitting. However, TiO_2 is limited because of its large band gap energy and fast electron-hole recombination [27]. To achieve better use of solar light, it has been intensely investigated the utilization of sensitizing dyes in various application areas such as photovoltaics, photocatalysis, and photoelectrochemistry [28]-[30]. MPcs as sensitizer are well-known for their intense absorption in the wide solar spectrum [31]-[33] . In several studies, MPcs have been used to improve PEC reactions by enhancing visible-light absorption and photoconversion. Y. Kawai et al. reported PEC system containing ITO/ZnPc/C60-Pt as a photocathode and WO_3 as photoanode and its utility for water splitting in the visible-light region [34]. B.D. Sherman et al. developed a tandem system for the generation of H_2 from hydroquinone by using a dye-sensitized photoelectrochemical cell and a dye-sensitized photovoltaic solar cell. They reported that the number of extra photons absorbed is almost double with phthalocyanine sensitizers [35].

A short time ago, we have introduced an unsymmetrical zinc phthalocyanine dye (**PCA-ZnPc-1**) which has three *tert*-butyl groups that act as electron-donating and chelating pyrazole-3-carboxylic acid as an alternative anchoring group to carboxylic acid. **PCA-ZnPc-1** sensitized solar cell showed a better power conversion efficiency when compared the unsymmetrical zinc phthalocyanines bearing only carboxylic acid which was ascribed to the stronger binding ability of the pyrazole-3-carboxylic acid [36]. In this study, we have extended the our previous work [36] and synthesized a new unsymmetrical phthalocyanine, **PCA-ZnPc-2**, which has six hexylsulfanyl groups that act as electron-donating as well as to further prevent the aggregation of phthalocyanine when compared to **PCA-**

ZnPc-1 and the pyrazole-3-carboxylic acid group act as electron-withdrawing and also serve as an anchoring group onto TiO_2. Subsequently, **PCA-ZnPc-2** has been used as a photosensitizer in water splitting photoelectrochemical and dye-sensitized solar cells for the first time. In both applications, TiO_2 was coated on the indium tin oxide (ITO) or fluorine-doped tin oxide electrodes by using doctor-blade technique [37]-[38], and then these electrodes were deposited with **PCA-ZnPc-2** at very short time due to **PCA-ZnPc-2**'s stronger binding ability. Because of the binding feature of **PCA-ZnPc-2** which is attributed to the pyrazole-3-carboxylic acid anchoring group, it may also be used in similar applications.

B.2 Experimental

B.2.1 Materials and methods

IR spectra were recorded on a Thermo Scientific iS10 FT-IR (ATR sampling accessory) spectrophotometer and electronic spectra on a Shimadzu UV-2450 and 2600 UV-vis spectrophotometer. ^{1}H-NMR spectra were recorded on a Bruker Avance III 500 MHz spectrometer using TMS as an internal reference. Mass spectra were measured on a Bruker Microflex LT MALDI TOF-MS. Elemental analyses were performed on a Thermo FlashEA 1112.

All reagents and solvents were of reagent grade quality and were obtained from commercial suppliers. Indium tin oxide (ITO), fluorine-doped tin oxide (FTO) conducting glass substrate with a resistance of 15 Ω^{-2} (TCO22-15), transparent TiO_2 paste (Ti-nanoxide T/SP), sealing film (Surlyn, Meltonix 1170–25), N719 (Ruthenizer 535), platinum paste (Platisol T/SP), and I^-/I_3^- redox electrolyte (Iodolyte HI-30) were purchased from Solaronix. 4-nitrophthalonitrile, chenodeoxycholic acid (CDCA), tetrabutylammonium tetrafluoroborate ($TBABF_4$), ferrocene (Fc/Fc^+), were also purchased from Sigma-Aldrich. **1**, **2** and 4,5-bis(hexylthio)-1,2-dicyanobenzene were synthesized according to the published procedure [36], [39].

The dye loading amount was obtained by the absorbance of the dyes desorbed from the photoanode using 0.1 M NaOH solution in water/tetrahydrofuran (1/1, v/v). Cyclic voltammetry (CV) measurements were performed with a PARSTAT

2273 potentiostat utilizing a glassy carbon (GCE) as working electrode, a Pt disk as reference electrode and a Pt wire as counter electrode in 0.1 M solution of $TBABF_4$ in dimethyl sulfoxide (DMSO) containing 0.5 mM **PCA-ZnPc-2** at a scan rate of 0.050 V s^{-1}. The results were calibrated using Fc/Fc^+ redox couple as an external standard.

B.2.2 Fabrication and characterization of DSSCs

In DSSCs, the TiO_2 film composed of a double transparent layers was prepared to utilize the doctor-blade technique on an FTO, as reported previously [40]. Commercially available an I^-/I_3^- Iodolyte HI-30 electrolyte containing 30mM iodide/tri-iodide in acetonitrile and additives of ionic liquid (lithium salt, pyridine derivative and thiocyanate) were purchased from Solaronix. A few drops of Iodolyte HI-30 were used to fill the space between the photo-anode and cathode of small surface area test cells.

Photoanodes were prepared by plunged the TiO_2 films in 0.3 mM solution of dyes with or without 5 mM CDCA as the co-adsorbent in ethanol/tetrahydrofuran (1/1, v/v) at room temperature for 2 h. As a reference DSSC, the TiO_2 film was also dipped in a solution made of 0.5 mM N719 and 5 mM CDCA in ethanol/acetonitrile (1/1, v/v) for 6 h. The Pt counter electrode was obtained by casting platinum paste solution on FTO substrate. This Pt counter electrode was then assembled with the dye-sensitized photoanode using the sealing film. The average thickness of the double layer TiO_2 film was ~12 μm measured by a surface profiler (KLA Tencor P6).

The current density-voltage (*J–V*) characteristic values of the DSSCs were obtained under simulated AM 1.5G irradiation using a solar simulator (96000, Newport) attached to the potentiostat at room temperature. The working area of DSSCs was 0.196 cm^2. The irradiance of 100 mW cm^{-2} was approximated using a calibrated silicon detector (918D-SL-OD3, Newport). IPCE spectra of the DSSCs were measured with a monochromator (74004, Oriel). EIS measurements were recorded by the potentiostat at an applied bias corresponding to the open circuit voltage (VOC) of each DSSC in the dark.

B.2.3 Preparation of photoelectrodes and photoelectrochemical measurements

The photoelectrodes were prepared by one-step doctor-blade technique [41]. Briefly, 0.5 g TiO_2 powder with 0.1/1.0 mL acetylacetone/water obtained a viscous paste. Then, 1.7 mL of water slowly added and was dropped 1 drop of Triton X-100 to paste. The paste was polished on an indium tin oxide (ITO) glass with dimensions of 1.5 cm × 1.5 cm and dried at 100 °C for 10 min. After, the film was annealed in an oven at 450 °C for 30 min.

The obtained ITO/TiO_2 photoanode was fabricated as follows: 1.0 mg **PCA-ZnPc-2**, 5.0 mL tetrahydrofuran and 5.0 mL ethanol were mixed by sonication for 5 min to solve. ITO/TiO_2 photoanode was immersed in the solution of **PCA-ZnPc-2** and was waited to obtain film of different thickness (1 s, 5 s, 1 min, 5 min, 30 min, and 1 h). ITO/TiO_2-**PCA-ZnPc-2** photoanode was dried at 100 °C for 5 min.

Photoelectrochemical measurements were performed with our homemade electrochemical cell for which a Max-303 Xenon Light Source 300 W (≥ 420 nm) was used at focused light intensity of 100 $mWcm^{-2}$. The light intensity of the light source was measured by using a light meter (HD 2302.0). Three-electrode system was used, in which ITO/TiO_2-**PCA-ZnPc-2** photoanode was a working electrode, Pt-wire and silver/silver chloride (Ag/AgCl) separated from the bulk of the solution by a double bridge were used as counter and reference electrodes, respectively. 25 mL of Na_2S (0.35 M)/Na_2SO_3 (0.25 M) aqueous solution was used as the electrolyte. The potential measured against Ag/AgCl reference electrode was converted to RHE potential (Eq. 1).

$$E_{(RHE)} = E_{Ag/AgCl} + 0.059pH + E^{\circ}_{Ag/AgCl} \quad (1)$$

Where $E_{Ag/AgCl}$ is working potential, $E^{\circ}_{Ag/AgCl}$ = 0.1967 V and *p*H of electrolyte is 13.0. *J*–*V* curves were recorded at a scan rate of 3.0 mV s^{-1} and the successive on-off illumination was used to examine transient photocurrents from 0.00 V to 1.50 V (vs. RHE) in the potential range. Photocurrent responses and open circuit potential responses were recorded at 0.0 V during on-off cycling (each 50 s).

B.2.4 Synthesis of 2

4-nitrophthalonitrile (340 mg, 1.975 mmol) and **1** (687 mg, 2.961 mmol) were dissolved in 75 mL dry DMF. Anhydrous potassium carbonate (360 mg, 2.625 mmol) was added to this solution in portions over 2 hours. The reaction mixture was stirred at room temperature during 3 days under Ar. The mixture was poured into ice-water (1.125 mL). The white precipitate was collected by filtration, dried under vacuum and then recrystallized from ethanol. Yield 588 mg (83.2%) M.p: 230 °C.

B.2.5 Synthesis of 3

2 (50 mg, 0.1396 mmol), 4,5-bis(hexylthio)phthalonitrile (150.8 mg, 0.4188 mmol), anhydrous $Zn(CH_3COO)_2$ (25.6 mg, 0.1396 mmol) and a few drops of DBU were refluxed in n-pentanol (3 mL) for 24 h under an argon atmosphere. The cooled reaction mixture was poured into ethanol (30 mL) and the precipitate was filtered off and washed with ethanol. The green solid was loaded on a silica gel column, then eluted by dichloromethane/ethanol mixtures of increasing polarity. The symmetric derivative of bis(hexylthio) substituted phthalocyanine was first eluted (eluent 150/1), and then the phthalocyanine **3** was collected (eluent 70/1) as a green solid. Yield: 31.5 mg (14.61%). ATR-IR (υ, cm^{-1}): 3075 (CH, aromatic), 2954-2851 (CH, aliphatic), 1723 (C=O). ^{1}H-NMR ($CDCl_3$): δ, ppm 8.72-7.10 (br, Ar-H, 14H), 4.32 (br, -OCH_2, 2H), 3.33 (br, -SCH_2, 12H), 2.34-0.89 (m, aliphatic -CH_2 and -CH_3, 75H). MS (MALDI-TOF): *m/z* 1544.133 $[M]^+$. UV-vis (THF, 10^{-5}) λ_{max} nm (log ε): 361 (4.67), 627 (4.36), 697 (5.12). Anal. calcd for $C_{83}H_{104}N_{10}O_3S_6Zn$: C, 64.42; H, 6.77; N, 9.05 (%). Found: C, 64.49; H, 6.85; N, 9.11 (%).

B.2.6 Synthesis of PCA-ZnPc-2

To a solution of **3** (31.5 mg, 0.0204 mmol) in THF (5 mL) was added 1 M NaOH (1.2 mL). The mixture was stirred at 60 °C for 48 h and monitored by TLC (dichloromethane/ethanol, 40/1). After completion, the reaction mixture was cooled to room temperature and concentrated to a small volume (approx. 1-2 mL) then acidified to pH: 2 by diluted HCl and diluted with water. The green

precipitate was collected by centifiguration, washed with water and dried under vacuum. Yield: 30 mg (99.7%). ATR-IR (υ, cm^{-1}): 3188 (NH), 2953-2852 (CH, aliphatic), 1704 (C=O). MS (MALDI-TOF): *m/z* 1474.532 $[M]^+$. UV-vis (THF, 10^{-5}) λ_{max} nm (log ε): 361 (4.73), 627 (4.48), 697 (5.22). Anal. calcd for $C_{78}H_{94}N_{10}O_3S_6Zn$: C, 63.41; H, 6.41; N, 9.48 (%). Found: C, 63.53; H, 6.37; N, 9.42 (%).

B.3 Results and Discussion

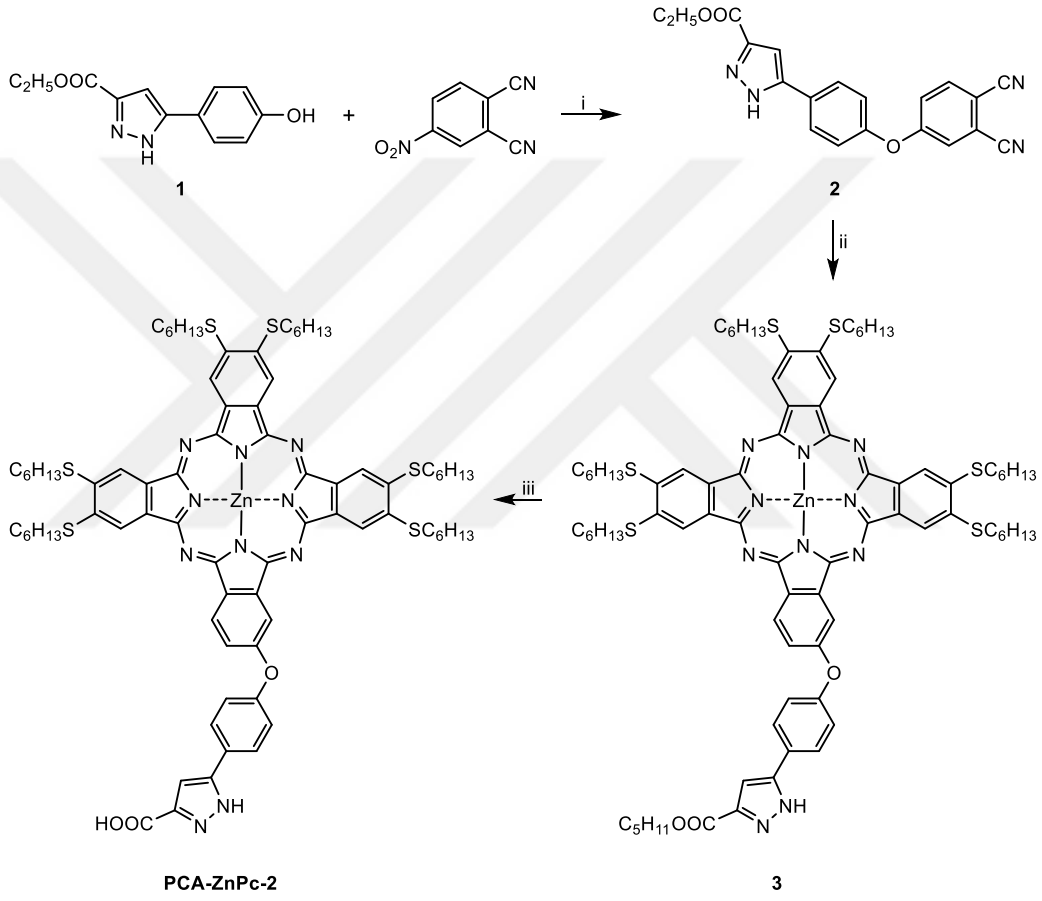
B.3.1 Syntheses and structural characterizations

In this study, new AB_3 type asymmetric pyrazole-3-carboxylic acid substituted zinc phthalocyanine **PCA-ZnPc-2** was synthesized by hydrolysis of ester group belonging to **3** with NaOH in THF. **3** was obtained by mixed cyclotetramerization method from phthalonitriles **2** [36] and 4,5-bis(hexylthio)-1,2-dicyanobenzene [39] in the presence of $Zn(CH_3COO)_2$, DBU in pentanol. Under these reaction conditions, a transesterification of the ethyl ester functions to the corresponding pentyl ester **3** was observed [42], [43] (Scheme 1).

New compounds were fully characterized with various spectroscopic techniques such as FT-IR, MS, ^{1}H-NMR, UV-vis, and elemental analysis. In the FT-IR spectrum of new compounds, for **3**; the disappearance of C≡N vibration and presence of C=O peak at 1723 cm^{-1}, for **PCA-ZnPC-2**; the presence of characteristic broad stretching vibration of carboxylic acid O-H at 3200-2500 cm^{-1}, NH peak at 3188 cm^{-1} belonging to pyrazole ring and C=O peak at 1704 cm^{-1} were observed. The shift of the C=O peak from 1723 cm^{-1} to 1704 cm^{-1} indicated that hydrolysis has taken place. MALDI-TOF MS spectrum is very important for verifying the structure in unsymmetrical phthalocyanines. In the MALDI-TOF MS spectrum, only the molecular ion peaks were observed at *m/z* 1544.133 for **3** and at *m/z* 1474.532 for **PCA-ZnPc-2** (Fig. S1-2).

The electronic absorption spectrum of metallated phthalocyanine shows two characteristic bands: the Soret band near 340 nm and a single Q band between 600 and 800 nm due to a π-π^* ligand transition. These two bands are dependent on the electronic interactions between the ligand as well as by the state of the

central atom and peripheral substitution [2], [4]. UV-vis absorption spectra were recorded for the unsymmetrical phthalocyanines **3** and **PCA-ZnPc-2** in THF. Compound **3** and **PCA-ZnPc-2** showed the single Q band and the same Soret band. Soret band values of **3** and **PCA-ZnPc-2** are 361 nm. The Q band values of zinc phthalocyanines **3** and **PCA-ZnPc-2** are 697 nm (Fig. S3). All these spectral results are compatible with structures.



Scheme B.1 Synthesis of **PCA-ZnPc-2**. (i) K_2CO_3, DMF, room temperature, 3 days; (ii) 4,5-bis(hexylthio)-1,2-dicyanobenzene, $Zn(CH_3COO)_2$, DBU, n-pentanol, 24 hours; (iii) 1 M NaOH, THF, 60 °C, 48 hours.

B.3.2 Optical and electrochemical properties

The UV–vis spectra of dyes in tetrahydrofuran (THF) consist of a Soret-band (300–400 nm) and a sharp and intense Q-band (650–750 nm) (Figure B.1a). Compared with **PCA-ZnPc-1**, **PCA-ZnPc-2** shows a noticeable red shift for the Q-band (Table

1, Figure B.1a). This spectral change can be attributed to a better electron-donating ability of the hexylsulfanyl groups than the *tert*-butyl groups, which is favorable for light harvesting (Figure B.2) [44]. Figure B.1b shows the absorption spectra of **PCA-ZnPc-2** adsorbed on the TiO_2 surface with and without 5 mM CDCA as a co-adsorbent. Without CDCA, the adsorbed dye shows a broadened and red-shifted Q-band as well as a new band at around 640 nm with respect to that in solution, indicating the formation of both J-and H-aggregation on the TiO_2 surface [45]. However, the ratio (R) of the intensity of new band (arising from H-aggregates) and the Q-band (arising from monomers) for **PCA-ZnPc-2** (0.67) are lower than that of **PCA-ZnPc-1** (0.93) [36]. Moreover, there is no obvious difference in R for **PCA-ZnPc-2** upon the addition of CDCA. These results indicate that the dye aggregation can be suppressed by introduction of the long alkyl chain groups into the phthalocyanine backbone (Fig. S4-5). This is consistent with the theoretical calculations and literature [12], [46]. Wan and co-workers reported that replacement of hexyl groups with methyl groups in the dye reduce the interactions between dye molecules (aggregation) and the power conversion efficiency (PCE) of DSSC increased from 3.18% to 4.29% in the absence of CDCA [46]. Also, the position and the number of alkyl groups affects the planarity of the phthalocyanine dye so that the aggregation behavior of phthalocyanines having a planar or non-planar geometry may be different [47], [48]. The geometry optimization shows that the hexyl chains in **PCA-ZnPc-2** are located above and below the plane of the macrocycle. Therefore, the non-planar hexyl moieties disallow more compact packing of the dye molecules on the TiO_2 surface.

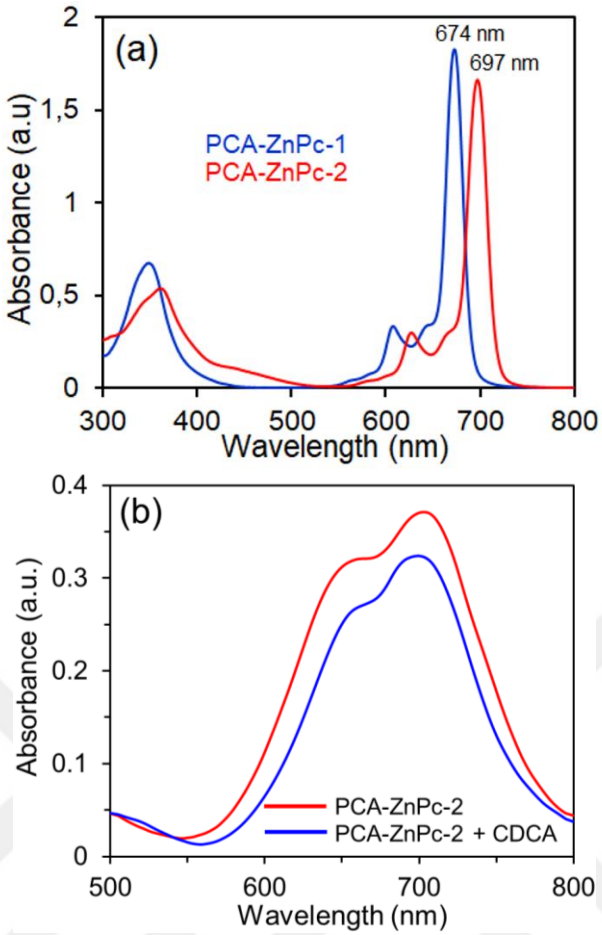


Figure B.1 Absorption spectra of the dyes in (a) THF solution (10^{-5} M) and (b) on TiO_2 film with and without CDCA.

Cyclic voltammetry was carried out to determine the electrochemical properties of **PCA-ZnPc-2** (Table 1). The oxidation potential (O_1) of **PCA-ZnPc-2** is assigned to its HOMO level. Compared to **PCA-ZnPc-1**, the incorporation of hexylsulfanyl groups slightly raises the HOMO level, indicating the stronger electron-donating ability of the dye (Hsieh et al., 2010). As also shown in Table 1, the HOMO and LUMO levels of **PCA-ZnPc-2**, compared to the redox potential of I^-/I_3^- (0.4 V *vs.* NHE) and the conduction band of TiO_2 (– 0.5 V *vs.* NHE), are suitable for dye regeneration and electron injection processes [50].

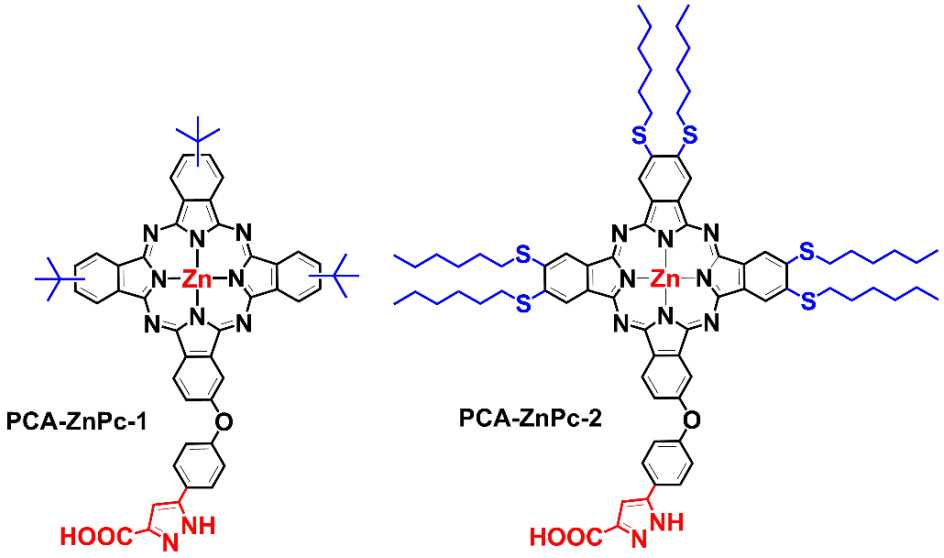


Figure B.2 Molecular structure of **PCA-ZnPc-1** and **PCA-ZnPc-2**.

Table B.1 Electro-optical properties of **PCA-ZnPc-2**.

Dye	λ_{abs} [nm][a] (ε [x 10^5 M^{-1} cm^{-1}][a])	λ_{onset} [nm][a]	λ_{em} [nm][a]	$\lambda_{abs}(TiO_2)$ [nm][b]	$E_{0\text{-}0}$ [eV][c]	E_{ox} [V][d]	E_{HOMO} [V][e]	E_{LUMO} [V][f]
PCA-ZnPc-2	697 (1.66)	716	713	705	1.73	0.55	1.18	– 0.55

[a] λ_{abs}: absorption wavelength;

ε: molar extinction coefficient;

λ_{onset}: absorption onset wavelength;

λ_{em}: emission wavelength. Recorded in THF solutions.

[b] $\lambda_{abs}(TiO_2)$: absorption maximum wavelength on the TiO_2 film.

[c] E_{0-0}: band gap, calculated using the equation $E_{0-0} = 1240/\lambda_{onset}$.

[d] E_{ox}: oxidation potential, referred to the external Fc/Fc^+ standard (0.34 V vs. Pt disk).

[e] E_{HOMO} (vs. NHE) was calculated by addition of 0.63 V to the E_{ox}.

[f] E_{LUMO} (vs. NHE) was obtained by $E_{HOMO}-E_{0-0}$.

B.3.3 Photovoltaic performance of DSSCs

Figure B.3a shows the photocurrent-voltage (J–V) curves of the DSSCs based on **PCA-ZnPc-2** with and without 5 mM CDCA, and the corresponding photovoltaic parameters, such as the open-circuit potential (V_{OC}), short-circuit current density (J_{SC}), fill factor (FF) and power conversion efficiencies (PCE), are summarized in

Table 2. In the absence of CDCA, for the DSSC based on **PCA-ZnPc-2**, compared to the DSSC based on **PCA-ZnPc-1**, PCE increased from 1.29% to 1.67%. The improved photovoltaic performance of **PCA-ZnPc-2** reflects the higher J_{SC}, attributable to the red-shift of the absorption spectrum of **PCA-ZnPc-2**. The higher J_{SC} could also be rationalized by the relatively lower dye aggregation on the TiO_2 surface due to the long alkyl chain groups [46]. When CDCA was added to the dye bath, the DSSC based on **PCA-ZnPc-2** shows a higher cell efficiency of 1.89%, as compared with that of 1.74% obtained for **PCA-ZnPc-1**. On the other hand, the PCEs for the DSSCs based on **PCA-ZnPc-1** and **PCA-ZnPc-2** improved by 35% and 13%, compared to the DSSCs without CDCA, indicating that the latter dye can suppress the aggregation [51].

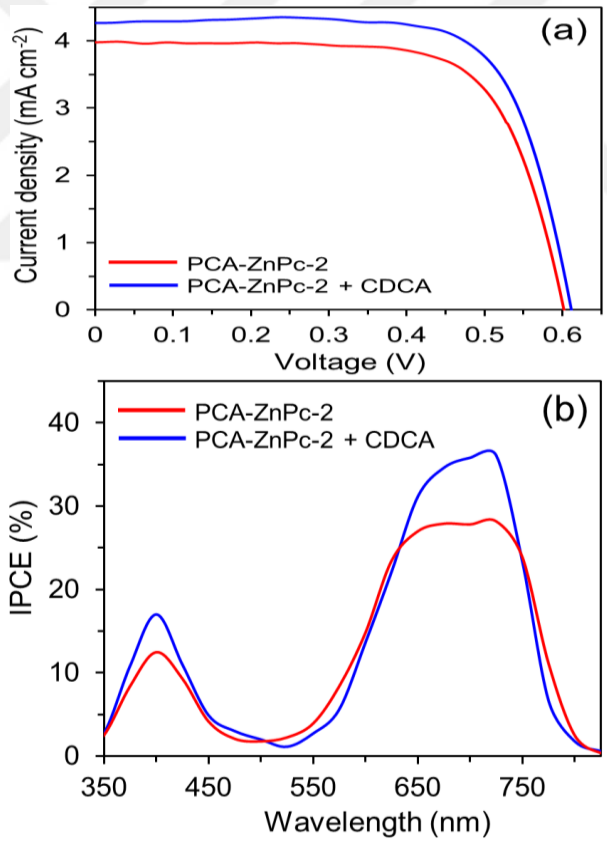


Figure B.3 (a) *J-V* curves and (b) IPCE spectra of DSSCs based on **PCA-ZnPc-2** with and without CDCA.

The IPCE spectra of the DSSCs based on **PCA-ZnPc-2** with and without co-adsorption of CDCA were also recorded to investigate the efficiencies for the conversion of sunlight to current at various wavelengths (Figure B.3b). Compared

with the solution spectrum, the IPCE spectra are broadened in the Q-band region, which are an agreement with the film spectra. The maximum value of the IPCE spectra increased slightly after the addition of CDCA, from 28% to 36%, which is consistent with the J–V curves. Evidently, CDCA is not necessary for **PCA-ZnPc-2** to improve efficiency. These results provide further evidence that the long alkyl chain groups suppress the dye aggregation in the absence of CDCA.

Table B.2 Photovoltaic parameters of the DSSCs.

Dye	IPCE integrated current density (mA cm^{-2})	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	PCE (%)	Dye loading amount (mol cm^{-2})
PCA-ZnPc-2	3.95	3.98	0.601	0.70	1.67	3.07×10^{-8}
PCA-ZnPc-2 + CDCA	4.29	4.27	0.611	0.72	1.89	2.76×10^{-8}
N719 + CDCA	-	14.95	0.781	0.68	7.94	-

To understand the CDCA effect on the V_{OC}, electrochemical impedance spectroscopy (EIS) analysis was performed in the dark. As shown in Figure B.4a, a large semicircle in the Nyquist plots is ascribed to the charge recombination resistance (R_{rec}) at the TiO_2/dye/electrolyte interface. The radius of the large semicircle increased in the order of **PCA-ZnPc-2** (151 Ω) < **PCA-ZnPc-2** + CDCA (169 Ω), which is good agreement with the V_{OC} values, **PCA-ZnPc-2** (0.601 V) < **PCA-ZnPc-2** + CDCA (0.611 V). These V_{OC} values are slightly lower than the DSSCs based on **PCA-ZnPc-1** due to their relatively lower dye loading amounts [52]. On the other hand, the V_{OC} values of DSSCs based on **PCA-ZnPc-1** and **PCA-ZnPc-2** with CDCA represent 23 mV and 5 mV of improvement compared to the DSSCs without CDCA, indicating that the latter dye is favorable for suppressing the aggregation and reducing the charge recombination [53]. Also, the insertion of CDCA plays to shift the conduction band of TiO_2 to more negative energy levels which consequently resulted in an increase in V_{OC}. The electron lifetimes (τ_e) for **PCA-ZnPc-2** and **PCA-ZnPc-2** + CDCA, which can be estimated by using equation $\tau_e = (2\pi f)^{-1}$ [54], where f is the frequency of the left peak in the Bode plots (Figure B.4b), are 13.06 and 18.41 ms, respectively, which is also consistent with their V_{OC} values. As a result, the CDCA coadsorbed with **PCA-ZnPc-2** onto the TiO_2 surface and effectively suppressed the recombination process by the more compact monolayer than does the adsorption of the dye alone, showed longer electron lifetime [55].

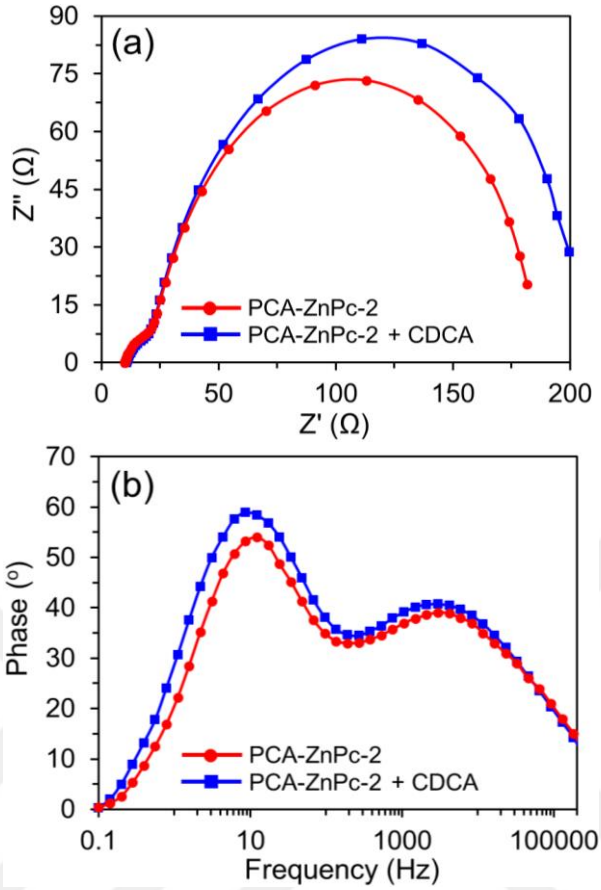


Figure B.4 (a) Nyquist and (b) Bode plots of DSSCs based on **PCA-ZnPc-2** with and without CDCA.

B.3.4 Photoelectrochemical studies

PEC cells supply a powerful means for converting light energy into chemical energy stored in molecules, for hydrogen production *via* water splitting. PEC cell comprised of a semiconductor photoanode and a Pt electrode as the cathode in the electrolyte solution. In this work, **PCA-ZnPc-2** as a photosensitizer, was fabricated on ITO/TiO_2. To obtain dye-sensitized photoelectrodes, they were deposited at specific waiting times and were tested for PEC hydrogen production. The results of PEC studies show that photoelectrodes indicated the best PEC performance at 5 seconds waiting time for **PCA-ZnPc-2** deposition. Therefore, all the PEC measurements were carried out on ITO/TiO_2-**PCA-ZnPc-2** (5s) photoelectrode. Briefly, events happening on the electrode surface as dye absorbs photons from incident light on the TiO_2. After absorbing, photosensitizer **PCA-ZnPc-2** are excited and photoelectrons are transferred into the CB of the TiO_2. The

transferred electrons move to electron collector (ITO), and then to counter electrode *via* an external circuit. After the cathodic reaction (for hydrogen gas production) takes place at the counter electrode (Pt). On the other hand, anodic reaction (oxidation) of sacrificial agent carries out into the VB of TiO_2 *via* holes. According to the above mentioned PEC performance measurements processes were carried out.

The open circuit potential (OCP) measurements were performed to determine the conductivity type of the electrodes (n-type or p-type) and to investigate the separation of photogenerated electrons-holes. As shown in Figure B.5, the OCP values were recorded under light illumination with intervals 50 seconds of on/off and calculated from the difference of potential under dark and light illumination [56]. The OCP value of the ITO/TiO_2-**PCA-ZnPc-2** photoelectrode was approximately 1.56 times higher than that of the ITO/TiO_2, indicating the remarkable charge separation of photoinduced carriers. In addition, the negative shift in the open-circuit voltage (V_{oc}) under irradiation indicates that ITO/TiO_2 and ITO/TiO_2-**PCA-ZnPc-2** photoelectrodes possess n-type conductivity as estimated.

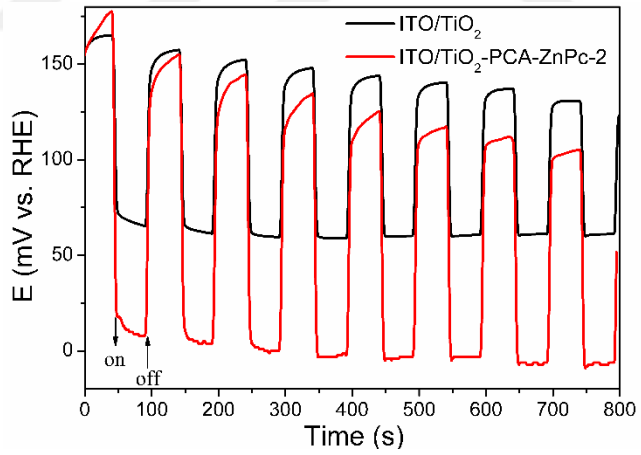


Figure B.5 Open circuit potential of ITO/TiO_2 and ITO/TiO_2-**PCA-ZnPc-2** versus RHE in S^{2-}/SO_3^{2-} electrolyte system.

PEC activities of ITO/TiO_2 and ITO/TiO_2-**PCA-ZnPc-2** photoelectrodes were predicted using the linear sweep voltammetry (LSV) technique. As shown in Figure B.6, the LSV response of ITO/TiO_2 and ITO/TiO_2-**PCA-ZnPc-2** photoelectrodes recorded in the dark and light illumination (50 seconds of on/off) at a scan rate of 3 mV s^{-1} for potential range from 0.00 V to 1.50 V versus RHE.

The PEC performance of prepared photoelectrodes from photocurrent response was calculated by using the difference in current densities in dark and light condition. The photocurrent response of the ITO/TiO_2-**PCA-ZnPc-2** photoelectrode is similar to that of ITO/TiO_2 photoelectrodes but overpotential of ITO/TiO_2-**PCA-ZnPc-2** photoelectrode is less. The PEC activity of the ITO/TiO_2-**PCA-ZnPc-2** photoanode in this study is comparable or somehow higher as compared to the reported dye-sensitized TiO_2 anodes [57]-[59].

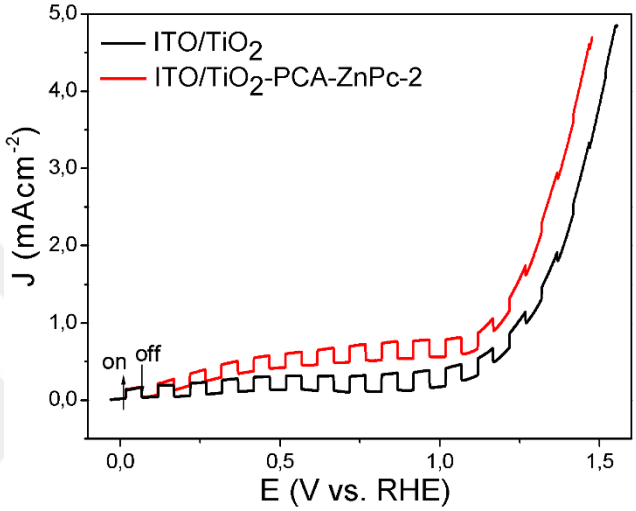


Figure B.6 Linear sweep voltammograms of ITO/TiO_2 and ITO/TiO_2-**PCA-ZnPc-2** versus RHE in S^{2-}/SO_3^{2-} electrolyte system.

Figure B.7 shows the current-time plots of ITO/TiO_2 and ITO/TiO_2-**PCA-ZnPc-2** photoelectrodes applied to 50 seconds of on/off cycles. These photoelectrodes indicated obvious photogenerated current responses to changes in light on/off states, without applied bias potential. The photogenerated current density of the ITO/TiO_2-**PCA-ZnPc-2** photoelectrode is higher than that of the ITO/TiO_2. The maximum photogenerated current response value of ITO/TiO_2-**PCA-ZnPc-2** (253.85 μAcm^{-2}) is almost one and a half times higher than ITO/TiO_2 (171.75 μAcm^{-2}). This result clearly demonstrates that the photogenerated current response of the ITO/TiO_2-**PCA-ZnPc-2** photoelectrode can be significantly enhanced with phthalocyanine photosensitizer. In addition, the current-time plot shows photostability of photoelectrodes. While ITO/TiO_2 photoelectrode indicates 6% loss of photostability, the ITO/TiO_2-**PCA-ZnPc-2** photoelectrode shows no loss of stability.

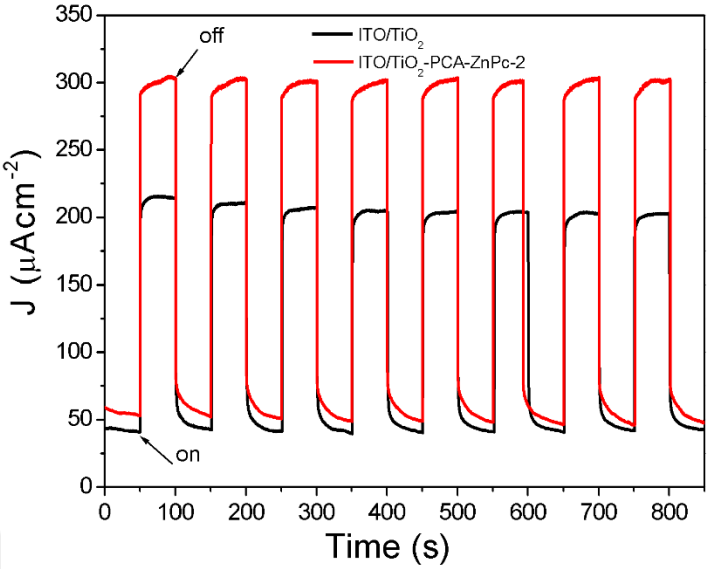


Figure B.7 Chronoamperometry plots of ITO/TiO_2 and ITO/TiO_2-**PCA-ZnPc-2** versus RHE in S^{2-}/SO_3^{2-} electrolyte system.

B.3.5. Theoretical calculations

Optimization of **PCA-ZnPc-2** molecule which has a Zn atom on its center was completed by Gaussian 09 in the gas phase [61]. DFT calculations were performed using the B3LYP hybrid exchange-correlation functional and the 6-311G(d,p) basis set [60]. The geometry optimization was followed by frequency calculations, and no imaginary frequencies were found. 3D structure of **PCA-ZnPc-2** was plotted and it was shown that pyrazole-phenoxyl and hexylsulfanyl groups perpendicular to the phthalocyanine ring as expected (Figure B.8).

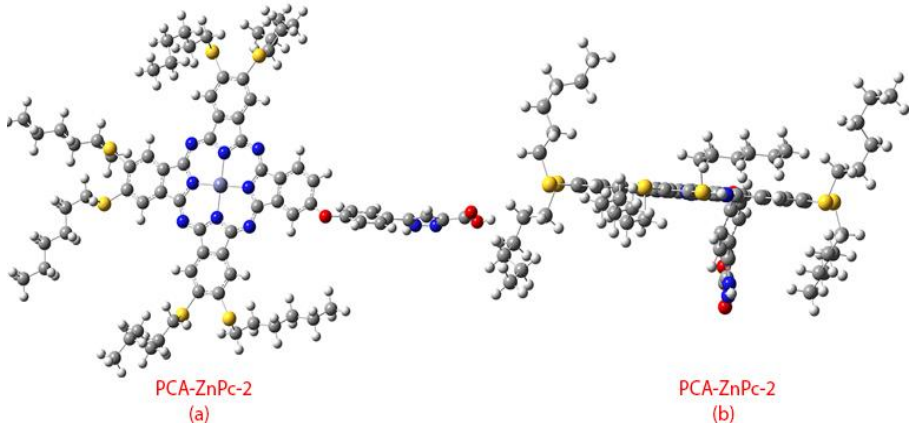


Figure B.8 Optimized structure of **PCA-ZnPc-2**: in front view (a) and side view (b).

HOMO (High Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) orbitals were plotted and their energies were calculated in eV (Figure B.9). Both HOMO and LUMO orbitals are localized on the phthalocyanine core and there is not any contribution of hexylsulfanyl groups on those frontier orbitals as seen in **PCA-ZnPc-1**. The addition of six hexylsulfanyl groups affected the band gap and the theoretical band gap was calculated as 2.14 eV which is lower than that of **PCA-ZnPc-1**.

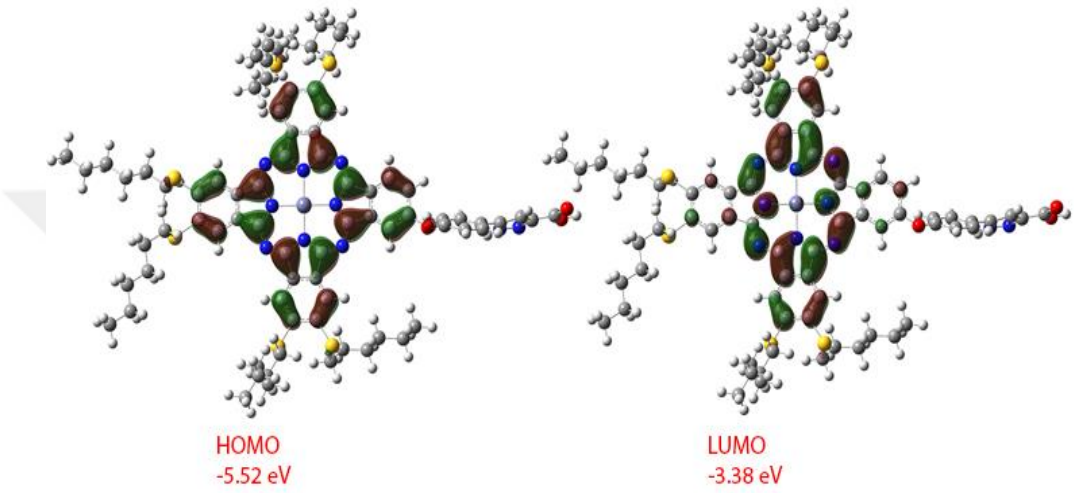


Figure B.9 HOMO and LUMO for **PCA-ZnPc-2**.

B.4 Conclusions

As a result, a new asymmetrically substituted zinc phthalocyanine (**PCA-ZnPc-2**) bearing a pyrazole carboxylic acid as the electron-withdrawing and anchoring group and six hexylsulfanyl as the bulky electron-donating groups was conveniently synthesized for DSSCs. The DSSC based on **PCA-ZnPc-2** showed a higher power conversion efficiency of 1.89%, as compared with that of 1.74% obtained for **PCA-ZnPc-1** with co-adsorbent. This might be attributed to the higher electron-donating ability and non-aggregated feature of **PCA-ZnPc-2** when compared to **PCA-ZnPc-1**. Also, the dye-sensitized PEC cell (ITO/TiO_2-**PCA-ZnPc-2** photoelectrode) exhibited a significant improvement in current density which is much better than that of the individual ITO/TiO_2 photoelectrode. The OCP measurements revealed that ITO/TiO_2-**PCA-ZnPc-2** photoelectrode has n-type conductivity and so, it has the potential to utilize as a photoanode in the visible region.

Acknowledgements

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Appendix A: Supplementary Material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.solener.2019.09.043.

B.5 References

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NON-AGGREGATING ZINC PHTHALOCYANINE SENSITIZER WITH BULKY DIPHENYLPHENOXY DONOR GROUPS AND PYRAZOLE-3-CARBOXYLIC ACID ANCHORING GROUP FOR COADSORBENT-FREE DYE-SENSITIZED SOLAR CELLS

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Abstract

A novel unsymmetrical zinc phthalocyanine complex (**PCA-ZnPc-3**) containing six 2,6-diphenylphenoxy donor groups and pyrazole-3-carboxylic acid anchoring group has been synthesized and used as a sensitizer for dye-sensitized solar cells (DSSCs). The optical, electrochemical and photovoltaic characteristics were evaluated and compared with the dyes containing the same anchoring group and *tert*-butyl (**PCA-ZnPc-1**) or hexylsulfanyl (**PCA-ZnPc-2**) donor groups, developed by our group. The DSSC with **PCA-ZnPc-3** exhibited a higher power conversion efficiency (PCE) of 2.04% as compared to that of **PCA-ZnPc-1** (PCE = 1.74%) and **PCA-ZnPc-2** (PCE = 1.89%). This enhancement in efficiency may be ascribed to the less dye aggregation and appropriate dye coverage. These results suggest that the incorporation of 2,6-diphenylphenoxy into pyrazole-3-carboxylic acid-based zinc phthalocyanine sensitizers can improve photovoltaic performance of DSSCs.

Keywords: Dye-sensitized solar cell, phthalocyanine, pyrazole-3-carboxylic acid, 2,6-diphenylphenoxy donor group

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C.1 Introduction

One of the most important scientific and technological research topics of this century is to replace fossil fuels with renewable energy sources. Among this energy sources, solar energy has an important place in terms of sustainability. Since the report by Gratzel in 1991, DSSCs utilizing nanoporous TiO_2 electrode have been attracted much attention because of their low cost in comparison with silicon-based photovoltaic devices [1]. Polypyridyl-ruthenium complexes (**N3**, **N719**) with a PCE of up to 12% are the most successful dyes in this field [2]. However, ruthenium-based dyes have disadvantages such as lack of absorption in the red/near-infrared region, their high cost, and the rarity of the metal [3]. To produce highly efficient DSSCs, sensitizers are required to absorb red/near-infrared region of solar spectrum [1].

Phthalocyanines are very convenient sensitizers for DSSCs because of their light absorption in the UV and red/near-infrared region, high extinction coefficients, photochemical and thermal stability [4], [5]. Therefore, many symmetric phthalocyanines have been used or tested as sensitizers in DSSC but they have showed low PCEs due to dyes' aggregation and solubility problem in organic solvents. In order to prevent such problems, unsymmetrical phthalocyanines bearing bulky aliphatic or aromatic donor groups and "anchoring group", i.e., a chemical substituent able to adsorb the dye molecule onto the TiO_2 surface, have been used in DSSCs [6]. At short intervals in 2007, two unsymmetrical zinc phthalocyanines, **PCH001** and **TT1**, having three *tert*-butyl donor groups and different anchoring group (succinic acid for **PCH001**, carboxylic acid for **TT1**),

were reported [7], [8]. With **PCH001** and **TT1**, the highest power conversion efficiencies were obtained in phthalocyanine-sensitized solar cells for that time (**PCH001** 3.05%, **TT1** 3.52%). After this reports, a large number of ABBB type unsymmetrical zinc phthalocyanine dyes with different bulky donor groups and anchoring group have been tested for DSSCs. Although unsymmetrical zinc phthalocyanines have less tendency to aggregation as compared to their symmetric derivatives, coadsorbent have been still used to prevent dye aggregation on TiO_2 surface [9]. However, the necessary amount of coadsorbent per dye molecule to reach the optimal efficiency is usally huge, which constitutes a major drawback because it reduces the total number of adsorbed dye molecules on the surface thus the absolute amount of injected electrons from the excited-dye to the electrode, which in fine limits the current density of the cell [10]. In 2010, Mori et al. reported a new unsymmetrical zinc phthalocyanine containing 2,6-diphenylphenoxy groups (**PcS6**), succeeding in completely prevent to aggregation without using a coadsorbent [11]. They had achieved high power conversion efficiency (4.60%) using **PcS6** for DSSCs. This unsymmetrical phthalocyanine derivative had been a new breakthrough for phthalocyanine-sensitized solar cells, and many phthalocyanine derivatives bearing 2,6-diphenylphenoxy groups have been synthesized and used for DSSCs. Phthalocyanine derivative containing 2,6-diphenylphenoxy donor groups reported by Ragoussi et al in 2012, has highest power conversion efficiency among DSSCs using phthalocyanine dyes.

A short time ago, we have reported phthalocyanine dyes, **PCA-ZnPc-1** and **PCA-ZnPc-2**, having three *tert*-butyl and six hexylsulfanyl donor groups, respectively, and pyrazole-3-carboxylic acid anchoring group. Pyrazole-3-carboxylic acid has two N-donors on the pyrazole ring and two O-donors on the carboxylate and this N and O atoms can chelate very stable with metal ions [12], [13]. Thus, electron injection efficiency of the dye and stability of the cell can be increased using pyrazole-3-carboxylic acid anchoring group in phthalocyanine-sensitized solar cells. It has been seen that **PCA-ZnPc-1** had 2.5 times higher power conversion efficiency with respect to **TT4** bearing *tert*-butyl donor groups and carboxylic acid anchoring group. However, utilizing chenodeoxycholic acid (CDCA) as coadsorbent was necessary to reach maximum PCE for **PCA-ZnPc**-1 and **PCA-ZnPc-**

2 sensitized solar cells. In this study, to eliminate the above-mentioned problems caused by the use of coadsorbent CDCA, we have synthesized new unsymmetrical zinc phthalocyanine, **PCA-ZnPc-3**, having six bulky diphenylphenoxy donor groups and pyrazole-3-carboxylic acid anchoring group and used as a sensitizer for DSSCs.

C.2 Experimental

C.2.1 Synthesis of 4-(4-(3-ethoxycarbonyl)-1H-pyrazole-5-yl) phenoxy) phthalonitrile [1]

4-nitrophthalonitrile (100 mg, 0.578 mmol) and 5-(4-hydroxyphenyl)-2*H*-pyrazole-3-carboxylic acid ethyl ester (201 mg, 0.867 mmol) were dissolved in 20 mL dry DMF. Anhydrous potassium carbonate (106 mg, 0.77 mmol) was added to the reaction solution in portionwise over 2 h. The reaction mixture was stirred vigorously at room temperature during 3 days under argon atmosphere. The mixture was poured into ice-water (300 mL). The white precipitate was collected by filtration, dried under vacuum and recrystallized from ethanol [14]. Yield 170 mg (82.1%), M.p: 230 ºC.

C.2.2 Synthesis of 4,5-bis(2,6-diphenylphenoxy)phthalonitrile [2]

4,5-dichlorophthalonitrile (200 mg; 1.015 mmol), 2,6-diphenylphenol (750 mg; 3.045 mmol) were dissolved in 5 mL anhydrous DMF and dry K_2CO_3 (1.4 g; 10.15 mmol) was added. Reaction mixture was mixed at 100 °C for 36 h. The mixture was cooled to room temperature and poured into ice-water. Then mixture was extracted with dichloromethane DCM (3x50 mL). Organic phase was dried over Na_2SO_4 and evaporated. The residue was purified by column chromatography using DCM as the eluent. Recrystallization from methanol gave white solid [9]. Yield: 286 mg (46%). ATR-IR (υ, cm^{-1}): 3072- 3035 (CH, aromatic), 2229 (C≡N). ^1H NMR ($CDCl_3$), (δ, ppm): 7.46 (6H), 7.42 (8H), 7.15 (4H), 7.06 (8H), 6.25 (2H).

C.2.3. Synthesis of 2,3,9,10,16,17-hexa(2,6-diphenylphenoxy)-23-mono(4-(3-(ethoxycarbonyl)-1H-pyrazole-5-yl)phenoxy)phthalocyaninatozinc(II) [3]

1 (45.8 mg, 0.128 mmol), **2** (236.4 mg, 0.384 mmol) were heated at reflux in n-pentanol (5 mL) under argon atmosphere for 72 h in the presence of $ZnCl_2$ (23.3 mg, 0.1705 mmol) and DBU (5 drops). After cooling to room temperature, reaction mixture was poured into methanol and resulting green precipitate was filtered off and washed with methanol. Afterwards, the green solid was purified by column chromatography on silica gel. Symmetric phthalocyanine with 2,6-diphenlphenoxy group was eluted first using DCM, and then **3** was eluted using DCM:ethanol (100:1). Yield: 30,6 mg (10.3%). ATR-IR (υ, cm^{-1}): 3055 (CH, aromatic), 2927 (CH, aliphatic), 1721 ($H_{11}C_5O$-C=O). MS (MALDI-TOF): *m/z* 2316.533 $[M]^+$. ^1H NMR ($CDCl_3$), (δ, ppm): 7.81-6,35 (Ar-H, 92H), 4.33 (2H), 3.34-3.10 (6H), 1.68 (3H). ^{13}C NMR ($CDCl_3$), (δ, ppm): 161.67, 148.70, 138.42, 138.29, 138.21, 137.58, 135.97, 135.91, 135.61, 135.08, 131.16, 131.10, 129.65, 129.58, 129.50, 129.27, 128.18, 127.89, 127.49, 127.32, 127.12, 127.04, 125.78, 107.80, 65.56, 38.02, 31.33, 22.27, 13.93. UV-vis (THF, 1 x 10^{-5} M) λ_{max}, nm (log ε): 681 (5.38), 614 (4.61), 358 (4.97).

C.2.4 Synthesis of 2,3,9,10,16,17-hexa(2,6-diphenylphenoxy)-23-mono(4-(3-(hydroxycarbonyl)-1H-pyrazole-5-yl)phenoxy)phthalocyaninatozinc(II) [PCA-ZnPc-3]

1 M NaOH (0.8 mL) was added to solution of **3** (30.6 mg; 0.013 mmol) in THF. The solution was mixed at 60 °C for 48 h. Then rection mixture was cooled to room temperature and evaporated to small volume (approx. 1-2 mL). Afterwards, the precipitate acidified to pH: 1-2 with diluted HCl and water was added. The green solids were collected by centifiguration, washed with water until neutralization and dried under vacuum. Yield: 12 mg (40.4%). ATR-IR (υ, cm^{-1}): 3055 (CH, aromatic), 1715 (HO-C=O). MS (MALDI-TOF): *m/z* 2246.177 $[M]^+$. ^1H NMR ($CDCl_3$), (δ, ppm): 7.81-6.35 (Ar-H, 92H). ^{13}C NMR ($CDCl_3$), (δ, ppm): 166.07, 151.67, 145.41, 137.30, 136.94, 135.86, 135.08, 135.01, 134.01, 131.30, 131.24, 131.12, 129.34, 129.28, 128.33, 128.27, 128.19, 128.13, 128.11, 127.93,

127.69, 127.49, 125.51, 110.36. UV-vis (THF, 1 x 10^{-5} M) λ_{max}, nm (log ε): 682 (5.36), 614 (4.59), 358 (4.94).

C.3 Results and Discussion

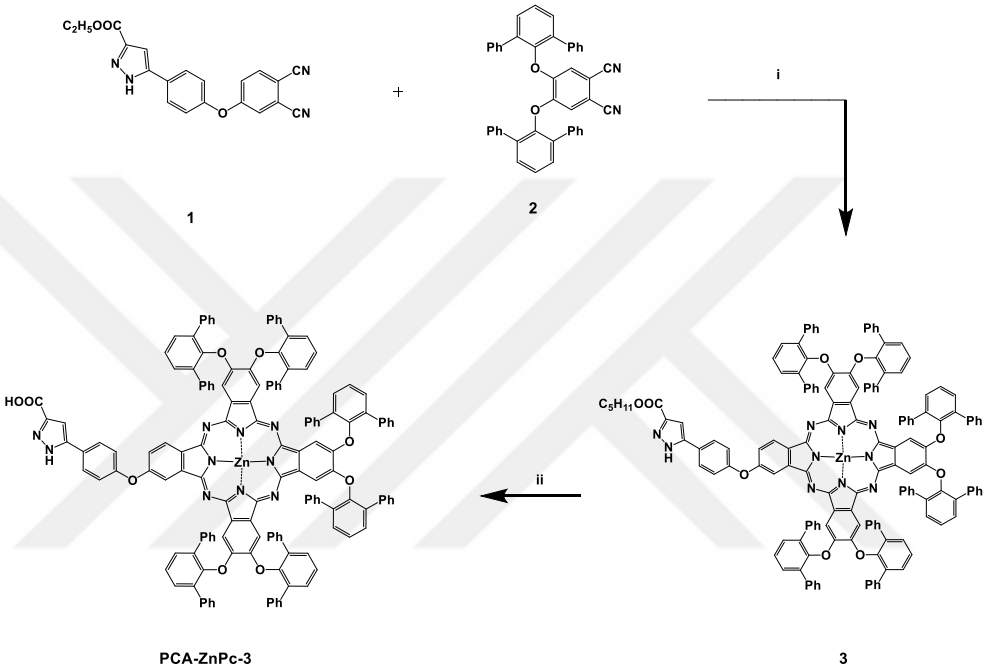
C.3.1 Synthesis and structural characterizations

In this study, firstly phthalonitrile derivatives **1** and **2** were synthesized according to the procedures described in the literature [9], [14]. Then compound **3** was obtained by mixed cyclotetramerization method from **1** and **2** in the presence of $ZnCl_2$ and DBU in pentanol at reflux temperature for 72 h. Under this reactions conditions, a transesterification was occured and pentyl ester form of the **3** was observed. Lastly, targeted molecule **PCA-ZnPc-3** was syhthesized by hydrolysis of the **3** (Scheme 1).

All of the new compounds were fully characterized with spectroscopic techniques such as ATR-IR, MALDI-TOF MS, ^{1}H NMR, ^{13}C NMR and UV-vis. In the ATR-IR spectrum of **3**, disappearence of the C≡N streching vibration and presence of the C=O stretching vibration at 1721 cm^{-1} support the structure. For **PCA-ZnPc-3** that synthesized by hydrolysis of **3**, C=O stretching vibration has shifted from 1721 cm^{-1} to 1715 cm^{-1} in the ATR-IR spectrum. In the MALDI-TOF MS spectra just molecular ion peaks were observed. Molecular ion peak of the **3** is at 2316.533. This result proves that transesterification has occured during the synthesis of the **3**. Molecular ion peak of the **PCA-ZnPc-3** is at 2246.177 amu (Fig. S1 and S2). When ^{1}H NMR and ^{13}C NMR spectra of the new compounds were examined, aromatic peaks were observed almost the same region. Peaks belonging to ester group were observed for compound **3** at 4.33, 3.34-3.10, 1.68 ppm in ^{1}H NMR spectrum and at 65.56, 38.02, 31.33, 22.27, 13.93 ppm in ^{13}C NMR spectrum. These peaks disappeared in the spectrum of the **PCA-ZnPc-3** as expected. Additionally, in the ^{13}C NMR spectra of the **3** and **PCA-ZnPc-3**; peaks belonging to pyrazole ring for **3** at 107.80 ppm and for **PCA-ZnPc-3** at 110.36 ppm were observed.

Metallophthalocyanines have two characteristic bands in electronic absorption spectrum. One is called the Q band in the visible region at 600-800 nm, The other

band is called Soret or B band between 300-400 nm in UV region. The reason for these two bands, π-π* transitions due to the 18 π-conjugated electrons [15]. UV-vis absorption spectra of the **3** and **PCA-ZnPc-3** were recorded in THF. **3** and **PCA-ZnPc-3** have same Soret band values at 358 nm. Q band values of **3** and **PCA-ZnPc-3** are at 681 nm and 682 nm, respectively. Obtained all spectral results are compatible with defined structures.



Scheme C.1. Synthesis of **PCA-ZnPc-3**. (i) $ZnCl_2$, DBU, n-pentanol, 72 h; (ii) 1 M NaOH, THF, 60 °C, 48 h.

C.3.2 Photophysical and electrochemical characteristics

The UV-vis spectrum of **PCA-ZnPc-3** bearing 2,6-diphenylphenoxy donor groups in tetrahydrofuran (THF) shows that it contains a Soret-band at 358 nm and a Q-band at 682 nm due to π-π* ligand transition (Figure C.1). The Q-band of **PCA-ZnPc-3** is red-shifted in comparison with **PCA-ZnPc-1** based on the *tert*-butyl donors [14], whereas this band is blue-shifted with respect to **PCA-ZnPc-2** based on the hexylsulfanyl donors [6]. Considering the three dyes have the same anchoring group (pyrazole-3-carboxylic acid), this result can be explained by the electron-donating ability of the 2,6-diphenylphenoxy group is between the *tert*-

butyl group and the hexylsulfanyl group. The absorption spectrum of the solid dye on TiO_2 exhibits slightly broadened and red-shifted by only 3 nm relative to that in solution, indicating low aggregation on the TiO2 (Matsuzaki et al., 2014). This can be attributed to the bulky 2,6-diphenylphenoxy moieties incorporated to the dye.

Cyclic voltammogram was measured to reveal the redox behaviors of **PCA-ZnPc-3** (Fig. S3 and Table 1) [16]. The oxidation potential (O_1) of the dye corresponding to the HOMO level is 1.20 V vs. NHE, which is lower than the potential of iodide/triiodide electrolyte (0.4 V vs. NHE), guaranteeing the dye regeneration [17]. Comparing these three dyes, the HOMO level of **PCA-ZnPc-3** is between the HOMO levels of **PCA-ZnPc-1** and **PCA-ZnPc-2**. In other words, the electron-donating ability of the 2,6-diphenylphenoxy group is better than the *tert*-butyl group and worse than the hexylsulfanyl group. The LUMO level of **PCA-ZnPc-3** was determined as –0.57 vs. NHE, which is higher than the conduction band of TiO_2 (–0.5 V vs. NHE), ensuring the sufficient electron injection [17].

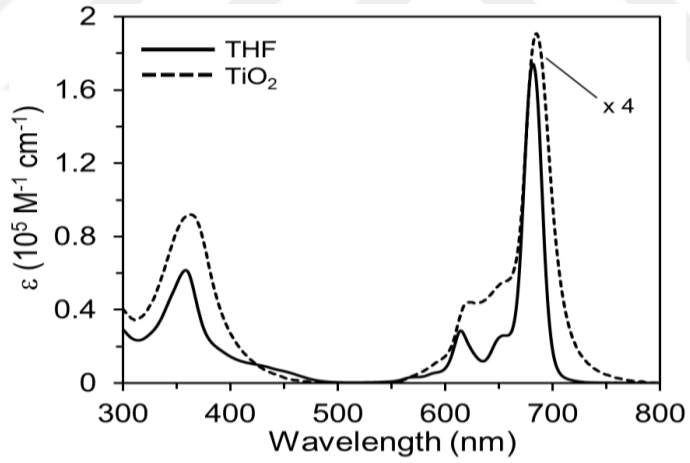


Figure C.1 Absorption spectra of **PCA-ZnPc-3** in THF (1 x 10^{-5} M) and on TiO_2 film.

Table C.1 Photophysical and electrochemical properties of **PCA-ZnPc-3**.

Dye	λ_{max} [nm] (ε [x 10^5 M^{-1} cm^{-1}])	λ_{onset} [nm]	$\lambda_{max}(TiO_2)$ [nm]	$E_{0\text{-}0}$ [eV][a]	HOMO [V][b]	LUMO [V][c]
PCA-ZnPc-3	358 (0.62), 682 (1.74)	702	685	1.77	1.20	–0.57

[a] $E_{0–0}$: band gap, estimated using the formula $E_{0–0} = 1240/\lambda_{onset}$.

[b] HOMO (vs. NHE) was taken from the oxidation potential of the dye solution in DMSO.

[c] LUMO (vs. NHE) was obtained by HOMO – $E_{0–0}$.

C.3.3 Photovoltaic properties

The photocurrent density–voltage (*J–V*) characteristics of the DSSCs based on **PCA-ZnPc-3** with and without chenodeoxycholic acid (CDCA) as the coadsorbent and the related photovoltaic characteristics i.e., short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and power conversion efficiency (PCE) were shown in Figure C.2a and Table 2. The device with **PCA-ZnPc-3** exhibited a higher PCE of 1.97% as compared to the devices based on our previous dyes **PCA-ZnPc-1** (PCE = 1.29%) and **PCA-ZnPc-2** (PCE = 1.67%). Similarly, for the cell based on **PCA-ZnPc-3**, compared with previous dyes, J_{sc} increased from 3.18 and 3.98 mA cm^{-2} to 4.64 mA cm^{-2}, while V_{oc} increased from 0.605 and 0.601 V to 0.624 V, respectively. Although the dye loading of **PCA-ZnPc-1** has higher than those of the others, the lower J_{sc} of **PCA-ZnPc-1** can be ascribed to the dye aggregation which quenches the excitons and inhibits electron injection [18]. In the presence of CDCA, the cell with **PCA-ZnPc-3** exhibits a higher PCE of 2.04% with a J_{sc} of 4.70 mA cm^{-2} and V_{oc} of 0.630 V. Under the same conditions, the cells with **PCA-ZnPc-1** and **PCA-ZnPc-2** showed inferior photovoltaic performances of 1.74% (J_{sc} = 3.18 mA cm^{-2}, V_{oc} = 0.628 V) and 1.89% (J_{sc} = 4.27 mA cm^{-2}, V_{oc} = 0.611 V). The PCE of the DSSC based on **PCA-ZnPc-3** achieves about 62% of the reference DSSC using **TT1** dye (3.31%). This result is probably attributed to the poor electronic communication due to the non-conjugated oxygen linker adjacent to the anchoring group [4]. According to the data, the addition of CDCA can

improve the PCE for the three dyes. The improvement is explained by the increase of both J_{sc} and V_{oc}. As previously reported [14], **PCA-ZnPc-1** showed 35% improvement in PCE as compared to that in the absence of CDCA, which may be due to the serious dye aggregation on TiO_2 [19]. In contrast to **PCA-ZnPc-1**, the PCEs for the DSSCs with hexylsulfanyl (**PCA-ZnPc-2**) and 2,6-diphenylphenoxy (**PCA-ZnPc-3**) donor groups improved by only 13% and 4% in the presence of CDCA, indicating that the aggregation may be weak or negligible for these dyes [19]. Evidently, it can be related to three-dimensional or bulky structure of donor groups in the latter dyes [20]. Generally, bulky groups may provide the ordered molecular arrangement and aggregate-free dye layer on the TiO_2 surface, resulting in higher J_{sc} [20]. Furthermore, these groups may lead to surface blocking effect through steric hindrance, suppressing the electron recombination, favoring higher V_{oc} [20]. Comparing the two dyes with bulky donor groups, the dye loading of **PCA-ZnPc-2** (2.76×10^{-8} mol cm^{-2}) is less than that of **PCA-ZnPc-3** (3.12×10^{-8} mol cm^{-2}), probably due to the linear structure of hexylsulfanyl groups in the former dye. The higher dye loading of **PCA-ZnPc-3** can not only improve the light-harvesting ability but also reduce the free volume for penetration of the redox electrolyte to the TiO_2, resulting in a higher J_{sc} and V_{oc} [21], [22]. As a result, the better photovoltaic performance of **PCA-ZnPc-3** relative to **PCA-ZnPc-2** is probably due to its higher dye loading amount.

Figure C.2b shows the incident photon-to-current conversion efficiencies (IPCE) as a function of the light excitation wavelength for the devices with **PCA-ZnPc-3**. As shown in Table 2, the photocurrent densities calculated by integrating the IPCE values (J_{sc}^{IPCE}) match well with J_{sc} values observed in the J–V curves, indicating the accuracy of the results. It can be also seen that the IPCE responses are in the range of 350–750 nm, which is in well agreement with the absorption spectrum on TiO_2 surface. The IPCE value of **PCA-ZnPc-3** was enhanced slightly with the addition of coadsorbent as compared to **PCA-ZnPc-1**, suggesting the bulky donor groups in the former can prevent dye aggregation [23], [24].

Table C.2 Photovoltaic parameters of the DSSCs.

Dye	J_{sc}^{IPCE} (mA cm^{-2})[a]	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)	Dye loading amount (mol cm^{-2})
PCA-ZnPc-3	4.45	4.64	0.624	0.68	1.97	3.35 x 10^{-8}
PCA-ZnPc-3 + CDCA	4.59	4.70	0.630	0.69	2.04	3.12 x 10^{-8}
TT1 + CDCA	–	7.58	0.615	0.71	3.31	–

[a] J_{sc}^{IPCE} values were integrated from their IPCE spectra.

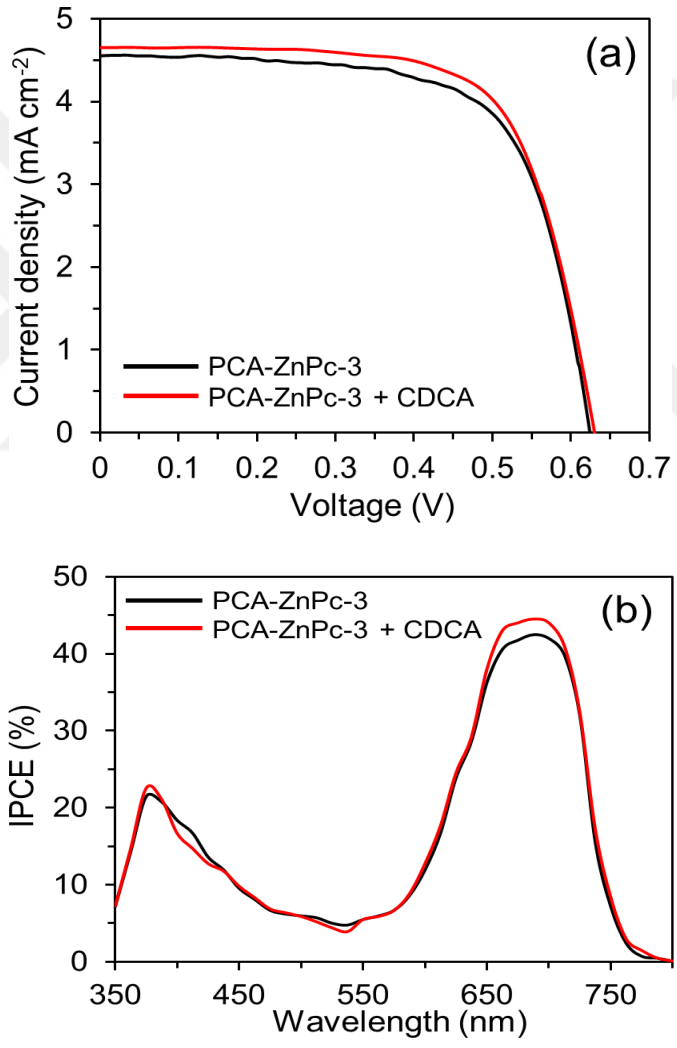


Figure C.2 (a) *J-V* curves and (b) IPCE spectra of the DSSCs with and without CDCA.

Electrochemical impedance spectroscopy (EIS) was employed to confirm the difference of V_{oc} between the DSSCs with and without CDCA in the dark at a

forward bias of −0.60 V. As shown in Figure C.3a, the radius of the larger semicircle at the low frequency region in the Nyquist plots expresses the charge recombination resistance (R_{rec}) at TiO_2/dye/electrolyte interface, which is related with V_{oc} value showed by the DSSC. The R_{rec} for **PCA-ZnPc-3 + CDCA** (46.7 Ω) is slightly higher than that of **PCA-ZnPc-3** (43.2 Ω). Similarly, the electron lifetimes (τ_e), which can be calculated by the peak frequency (f) in the low-frequency region in Bode plots using $\tau_e = 1/2\pi f$, are 7.1 and 8.9 ms for **PCA-ZnPc-3** and **PCA-ZnPc-3 + CDCA** (Figure C.3b). Obviously, both R_{rec} and τ_e are consistent with the sequence of V_{oc} values obtained in J–V curves.

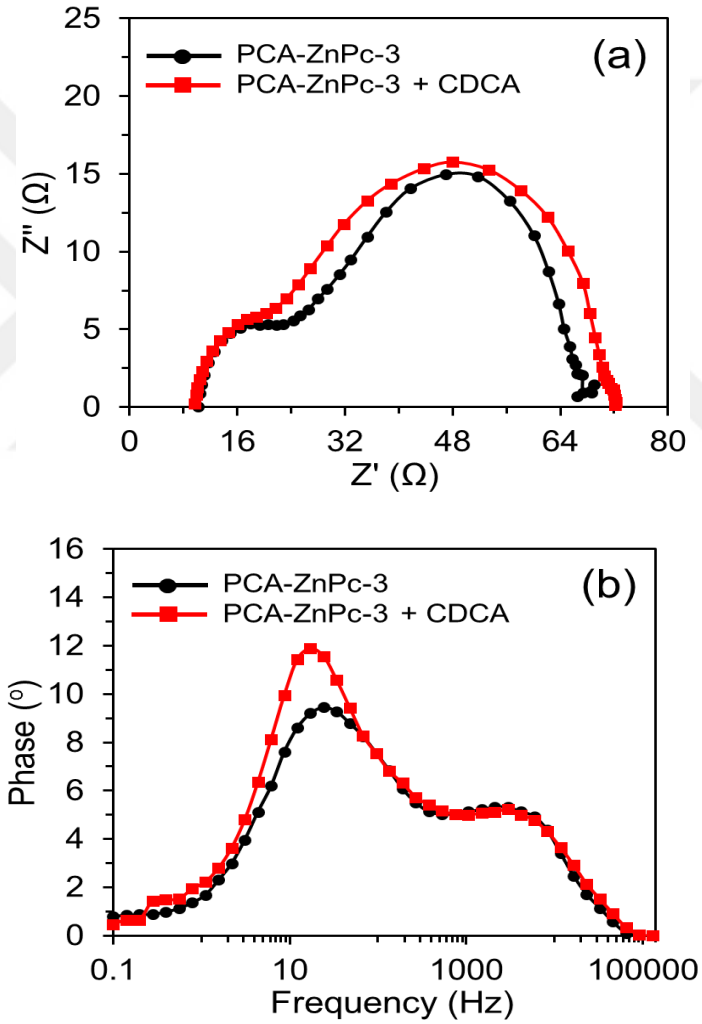


Figure C.3 (a) Nyquist and (b) Bode plots of the DSSCs.

C.3.4 Theoretical calculations

All optimizations were carried out by Gaussian 09 in the gas phase in which DFT calculations were utilized by using the B3LYP/6-311G(d,p) basis set [25]-[30].

Geometrically optimized structure of **PCA-ZnPc-3** uncovered that the phthalocyanine core is planar and perpendicular to the pyrazole unit. All diphenylphenoxy units are vertical to the phthalocyanine (Figure C.4).

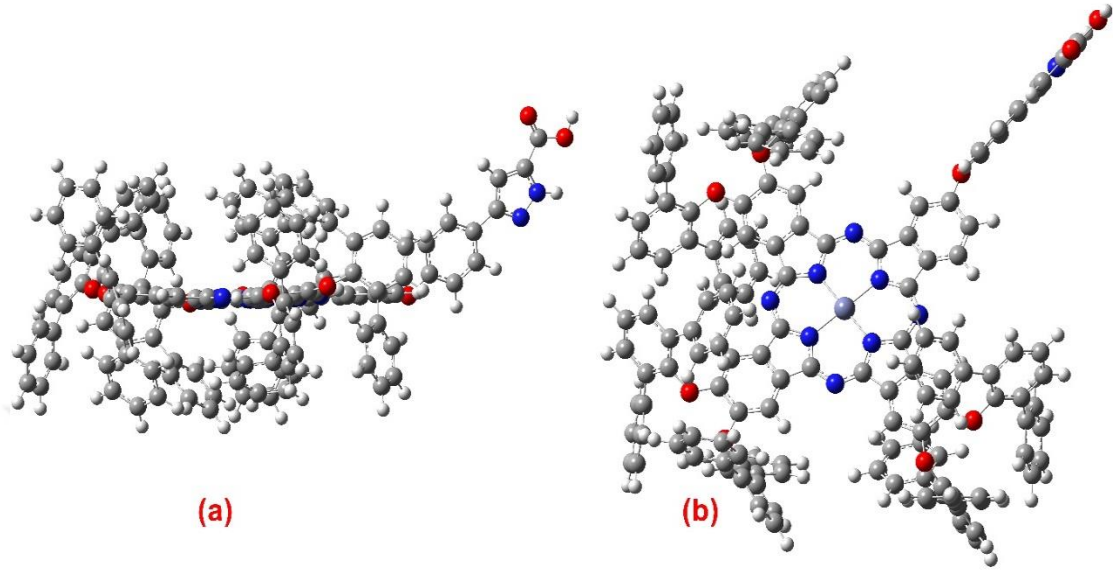


Figure C.4 Two different visions for **PCA-ZnPc-3**. (a) in front view; (b) side view.

Electron transfer between two important orbitals, HOMO and LUMO, is considered to understand solar cells' capacity in detail. Theoretical calculation and plotting of frontier molecular orbitals were, therefore, calculated using the same hybrid method. HOMO and LUMO of **PCA-ZnPc-3** were localized on the phthalocyanine skeleton with small differences (Figure 5). Although HOMO consists of all ZnPc frames, LUMO was restricted on the ZnPc unit except that two phenyl rings of ZnPc, perpendicular to the phenoxy-pyrazole group, did not give extreme contribution to LUMO. There are three phenoxy units that carry two identical phenyl rings attached to phthalocyanine. However, neither phenoxy-pyrazole-carboxylic acid unit nor phenoxy units did have a contribution to HOMO or LUMO orbitals. In our previous studies in which the pyrazole ring was used, we have seen almost the same theoretical band gap between 2.17-2.14 eV and the corresponding power conversion efficiency between 1.74 and 1.89%. These results showed that attached groups on the aromatic core, such as *tert*-butyl and hexylsulfanyl, did not change the solar cell's electronic capacity. However, in this study, we have advanced the yield of the cell up to 2.04%, although the band gap

calculated as 2.14 eV, did not change (Figure C.5). The increase of the cell yield might be due to bulky diphenylphenoxy units, which regulate the aggregation of molecules (Figure C.4). This was also proved with increasing V_{oc} value, which was found as 0.630 V in this study.

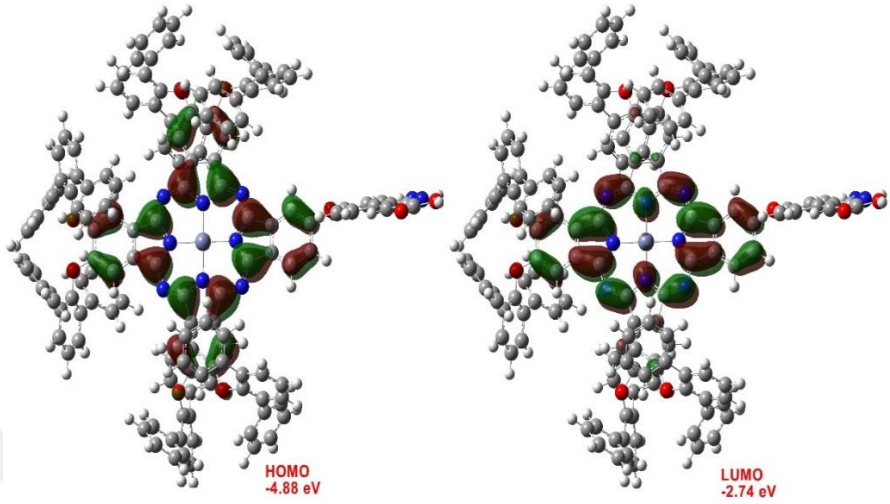


Figure C.5 HOMO and LUMO orbitals for **PCA-ZnPc-3**.

C.4 Conclusions

In this study, a push-pull zinc phthalocyanine dye (**PCA-ZnPc-3**) having 2,6-diphenylphenoxy donor groups and pyrazole-3-carboxylic acid anchoring group was synthesized for DSSCs. Both electronic absorption and electrochemical measurements have verified that the synthesized dye may be used as a sensitizer. It performed a higher power conversion efficiency of 2.04% (J_{sc} = 4.70 mA cm^{-2}, V_{oc} = 0.63 V, FF = 0.69) with respect to **PCA-ZnPc-1** (1.74%) and **PCA-ZnPc-2** (1.89%). The better photovoltaic performance of **PCA-ZnPc-3** may be attributed to its non-aggregation characteristics. These results confirmed that 2,6-diphenylphenoxy moiety is a promising donor group to improve photovoltaic performance of zinc phthalocyanine-based DSSCs.

Acknowledgements

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Appendix A. Supplementary Data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.solener.2021.08.033

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Projeler

1. Güneş Pili Uygulamaları İçin Yeni Boyar Maddelerin Sentezi ve Karakterizasyonu, Yıldız Teknik Üniversitesi BAPK Proje No: FDK-2018-3463, Araştırmacı

Ödüller

1. TÜBİTAK BİDEB 2211/C Yurtiçi Öncelikli Alanlar Doktora Bursu

2. YÖK 100/2000 Doktora Bursu