

Exploring the Role of Central Metals in Bulky Phthalocyanines for Dye-Sensitized Solar Cells

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Two series of metallo-(Zn(II), Mg(II), and Ru(II)) and free-base phthalocyanines (Pcs) with a carboxyl anchoring group and well-established bulky peripheral substituents (either tert-butyl or bulky 2,6-diisopropylphenoxy) were synthesized and tested as sensitizers in dye-sensitized solar cells (DSSCs). The trend of photovoltaic efficiencies (PCEs) for free-base and metallo Pcs followed the order Zn(II)Pc > Mg(II)Pc ≫ H2Pc ≈ Ru(II)Pc regardless of the peripheral substitution. Higher efficiencies (4.95 versus 3.63 for the Zn(II) derivatives) were achieved with Pcs bearing the bulkier 2,6-diisopropylphenoxy group, indicating a lower aggregation and more suitable HOMO-LUMO levels.

Furthermore, these derivatives showed a more relevant influence of the metal on the PCE values (from the highest 4.95 for the Zn(II)Pc to the lowest 0.23 for the Ru(II)Pc. In both series, the best PCEs observed with the Zn(II) derivatives were mainly due to their highest J_{sc} values. The lowest efficiencies found for the free-bases and Ru(II) derivatives were attributed to a mismatch between their LUMO levels and the conduction band of the TiO₂ and lower light-harvesting capabilities, respectively. In conclusion, Zn(II) derivatives are still the best Pc candidates to use as sensitizers in molecular photovoltaics.

Introduction

The development of organic dyes for dye-sensitized solar cells (DSSCs) has drawn much attention in recent years because of their notable advantages, such as low-cost of fabrication, low environmental toxicity, high molar absorption coefficients and

tunable optical properties through adequate molecular engineering.^[1,2] Impressive record power conversion efficiencies up to 13–14% have been accomplished with push-pull type porphyrin photosensitizer (SM315)^[3] and a cocktail of organic dyes (ADEKA-1/LEG4),^[4] respectively. Phthalocyanines (Pcs), synthetic analogues of porphyrins, show an extraordinary potential as sensitizers for DSSC applications because of their excellent light-harvesting ability with intense absorption in the visible and near-IR region of the solar spectrum, excellent photochemical and thermal stability and suitable redox features.^[5] For years, however, the efficiency of Pc-based DSSCs has been rather low, owing to issues related to high-aggregation behavior and poor electronic coupling between the Pc excited state and the conduction band (CB) of TiO₂.^[6] A significant breakthrough in this field occurred with the development of a new generation of Pcs based on highly soluble and less aggregated tri-tert-butyl-carboxyl-Zn(II)Pc derivatives with a push-pull structure.^[7] Device efficiencies as up to 3.5% were achieved using TT1 as sensitizer (Figure 1) and in the following years it has been investigated in depth the impact of different

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Supporting information for this article is available on the WWW under <https://doi.org/10.1002/chem.202400468>

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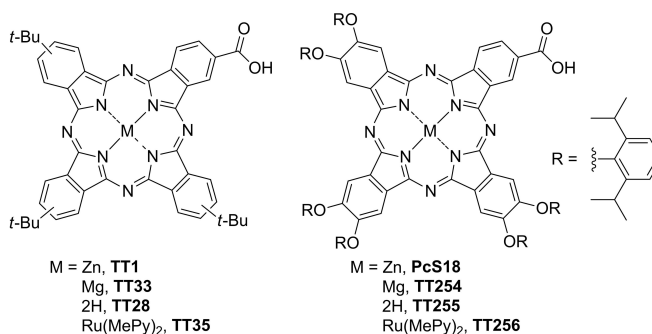


Figure 1. Molecular structures of carboxyphthalocyanines: TT1, TT28, TT33, TT35, TT254, TT255, TT256 and PcS18.

parameters on the photovoltaic performances of Zn(II)Pc-sensitized solar cells, such as the type of peripheral substitution, linker, number and nature of the anchoring group(s) and incorporation of co-adsorbent to reduce aggregation.^[8,9] The introduction of bulky substituents in the periphery of the macrocycle with the aim of suppressing aggregation turned out to be an important step forward in achieving higher device efficiencies. In 2010, Kimura's group reported remarkable efficiencies up to 4.6% with DSSC devices based on a non-aggregated carboxyl-Zn(II)Pc substituted at the periphery with six 2,6-diphenylphenoxy groups, highlighting the importance of suppressing aggregation of Pc dyes on TiO₂.^[10] Successive improvements on efficiencies were accomplished over the years with sensitizers **TT58** (5.6%),^[11] **PcS18** (5.9%)^[12] and **PcS20** (6.4%),^[13] which all possess six bulky 2,6-dialkyl- or 2,6-dialkoxyphenoxy units as peripheral substituents, and a carboxyl group directly attached to the macrocycle. Our research groups and other have also shown that a carboxyethynyl- instead of carboxyl- anchoring group in the molecular structure of these bulky substituted Pcs allows to achieve even higher conversion efficiencies, with a record PCE value of 6.5% obtained for a Pc-based DSSC with **TT40**.^[11,14]

It is well-established that the nature of the metal ion at the central cavity of the macrocycle affects the photophysical and electronic properties of the Pc. The most successful Pcs for DSSCs use Zn(II) as metal center, and the vast majority of the research^[6] in the field has been focused on i) the introduction of different motifs at either peripheral (β) or non-peripheral (α) positions of the macrocycle, and ii) the anchoring group(s) (nature, number and/or incorporation of spacer), but less attention has been addressed concerning the use of other metal ions. For instance, Ru(II)Pcs have attracted a great attention over the years as sensitizers for DSSC applications because of their remarkably low tendency to form aggregates since the Ru(II) metal center is strongly coordinated by axial ligands.^[15] In addition, optical properties of Ru(II)Pcs strongly depend on the axial substituent. However, despite of the good electron injection responses achieved by using Ru(II)Pcs incorporating anchoring groups at the axial position, devices efficiencies remained lower than 1%.^[16,17]

In this context, and inspired by the success of Zn(II)Pcs **TT1** and **PcS18** in DSSC, we decided to prepare two series of Pc sensitizers based on their respective designs that incorporate none (free-base) or other metal centers (Mg^{II} or Ru^{II}) (Figure 1). Accordingly, two series of tri-*tert*-butyl and hexa-(2,6-diisopropylphenoxy) phthalocyanines (Pcs) substituted with a carboxyl anchoring group directly attached to the Pc ring on the periphery were prepared, as free base (**TT28** and **TT255**, respectively), and their corresponding metal complexes, namely, Mg(II) complexes (**TT33** and **TT254**, respectively) and Ru(II) complexes (**TT35** and **TT256**, respectively). The photovoltaic performance in DSSCs of these two families of dyes were tested and compared to the corresponding Zn(II)-Pc benchmarks previously reported (**TT1** and **PcS18**). It is worth mentioning that these two benchmark dyes are tested and compared for the first time under the same conditions in the present work. All these Pc derivatives were chosen to gain

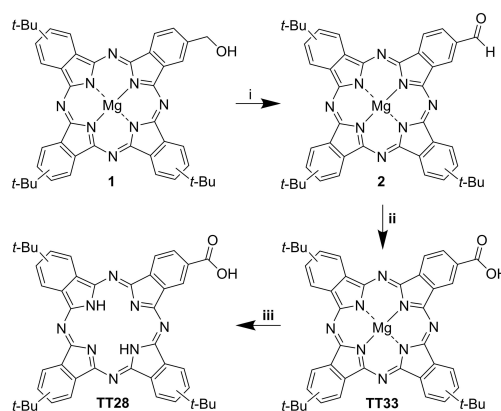
some insights into the basic requirements to guide the molecular engineering of new efficient Pc-based sensitizers.

Results and Discussion

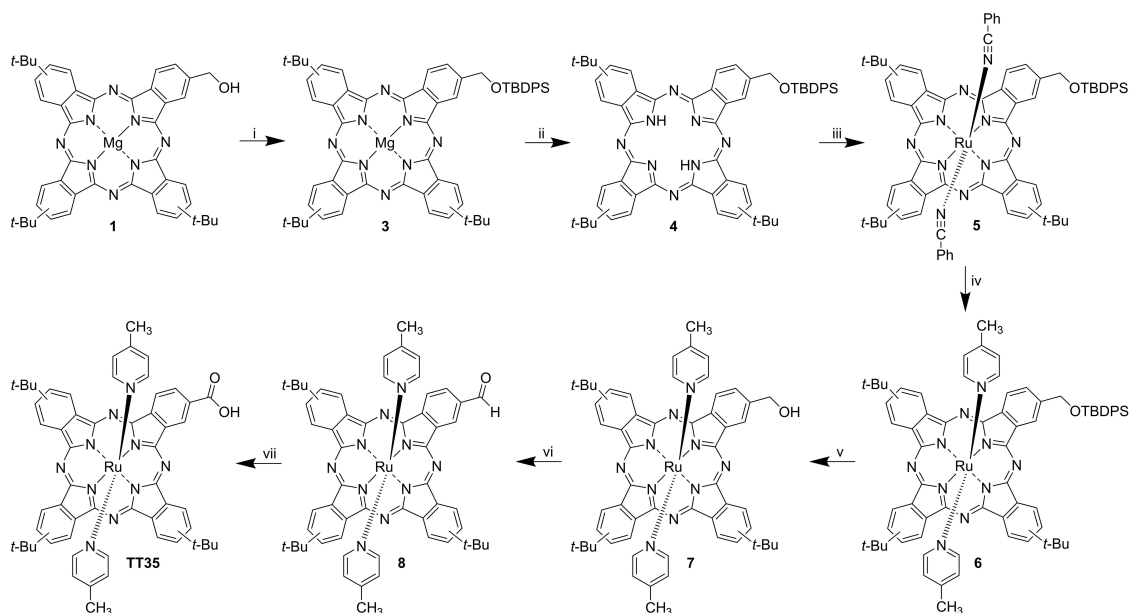
Synthesis of Tri-*tert*-Butyl Pcs

In the tri-*tert*-butyl Pc series, hydroxymethyl-substituted MgPc **1** is the key precursor for the preparation of **TT28** (2H), **TT33** (Mg^{II}) and **TT35** (Ru^{II}) (Schemes 1 and 2).

Mg(II)Pc **1** is prepared by standard statistical cross condensation of 4-*tert*-butylphthalonitrile and 4-hydroxymethylphthalonitrile in the presence of MgCl₂ salt as template in DMAE (the detailed synthetic procedures and characterization data are given in the Electronic Supporting Information). Mg(II)Pc **1** (mixture of regioisomers) was isolated from the reaction mixture by column chromatography in 21% yield. **TT33** was prepared by following the same synthetic route used for the preparation of benchmark dye **TT1**.^[7] Firstly, hydroxymethyl-substituted Mg(II)Pc **1** was subject to oxidation with periodane derivative IBX in DMSO to afford the corresponding formyl derivative **2** in almost quantitative yield, which was further reacted with NaClO₂ in the presence of sulfamic acid as scavenger to lead **TT33** in 74% yield. Free-base derivative **TT28** was prepared by demetallation of **TT33** in the presence of TFA in quantitative yield. Concerning Ru(II)Pc **TT-35**, a new synthetic strategy had to be developed. Indeed, one of the most convenient method for the preparation of Ru(II)Pcs consists in the metallation of the already preformed metal-free phthalocyanine using Ru₃(CO)₁₂ in refluxing benzonitrile, and following this synthetic approach, a myriad of Ru(II)Pcs has been successfully prepared for a wide range of applications.^[15] However, working with unsymmetrical Pcs bearing sensitive functional groups (*i.e.* hydroxy, carboxy) is more challenging, and indeed, the synthesis of Ru(II)Pc **TT35** from the corresponding free-base, either from carboxyl-(**TT28**) or hydroxymethyl-substituted Pc, resulted to be unsuccessful under these conditions. It turned out that the protection of the hydroxyl group before the ruthenium-



Scheme 1. Synthesis of **TT28** and **TT33**: (i) IBX, DMSO, rt, 3 h (91%); (ii) NaClO₂, NH₂SO₃H, THF/H₂O, 0 °C, 0.5 h (74%); (iii) CF₃COOH, CH₂Cl₂, rt, 5 h, (93%).



Scheme 2. Synthesis of **TT35**: (i) TBDPSCl, imidazole, DMF, 0 °C to rt, 16 h, (90%); (ii), (iii) CF₃COOH, CHCl₃, rt, 3 h, (93%); (iii) Ru₃(CO)₁₂, benzonitrile, 230 °C, 16 h, (55%); (iv) 4-methylpyridine, THF, 70 °C, 3 h, (88%); (v) TBAF 1 M in THF, THF, 0 °C, (66%); (vi) IBX, DMSO, rt, 3 h, (87%); (vii) NaClO₂, NH₂SO₃H, THF/H₂O, 0 °C, 0.5 h, (64%).

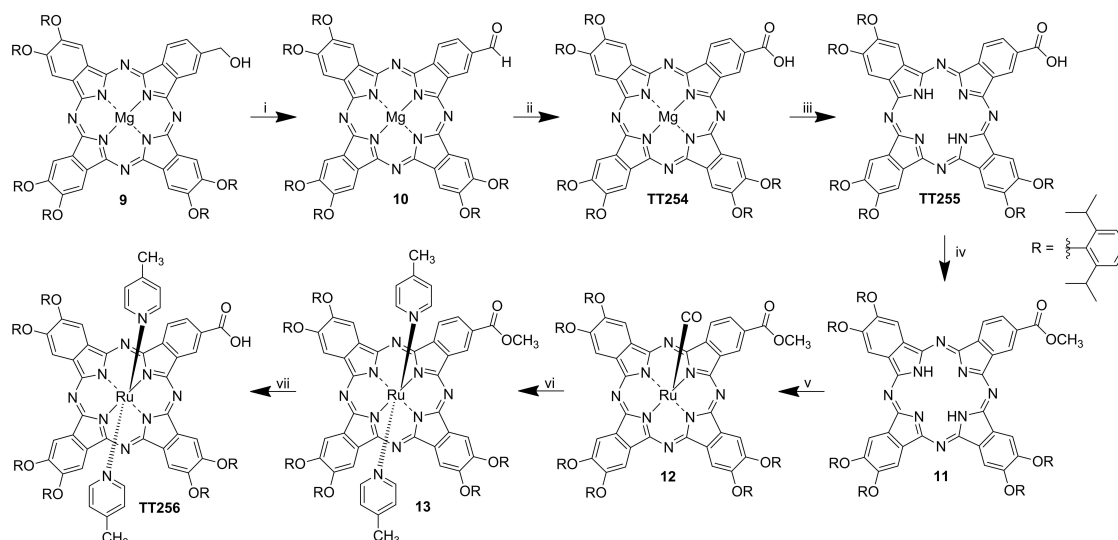
metallation step was necessary to obtain the corresponding Ru(II)Pc in good yield. To be feasible and compatible with the new synthetic route, a Mg-metallation/demetallation sequence was also required. Hence, we made use of MgPc **1** to prepare the Mg(II)Pc **3** intermediate, which was obtained by treating Mg(II)Pc **1** with *tert*-butyldiphenylchlorosilane and imidazole in 90% yield (Scheme 2). Then, compound **3** was demetallated in the presence of TFA to form H₂Pc **4** in quantitative yield. Compound H₂Pc **4** was then treated with Ru₃(CO)₁₂ in refluxing benzonitrile for 24 h to afford successfully Ru(II)Pc **5** in 55% yield after purification by column chromatography, highlighting the need of protecting the hydroxymethyl group before the ruthenation step. Replacement of the labile apical benzonitrile ligands by strongly coordinated 4-methylpyridine ones and further removal of the silyl group using TBAF led to key hydroxymethyl phthalocyanine Ru(II)Pc **7** in good yield. Finally, compound **7** was oxidized with the periodinane derivative IBX under very mild conditions to afford the formyl phthalocyanine Ru(II)Pc **8** in 87% yield, which was further reacted with NaClO₂ in the presence of sulfamic acid to lead **TT35** in 64% yield.

Synthesis of Bulky Pcs

The synthesis of the bulky versions Mg(II)Pc **TT254** (2 steps from hydroxymethyl-Pc **9**) and subsequent demetallation with TFA to afford the corresponding free-base **TT255** (Scheme 3), were carried out following the same synthetic procedures as described for the tri-*tert*-butyl analogues (*vide supra*). As well, the starting precursor hydroxymethyl-Pc **9** was obtained by statistical cross condensation using 4,5-di(2,6-diisopropylphenoxy)phthalonitrile instead of 4-*tert*-butylphtha-

lonitrile, and 4-hydroxymethyl phthalonitrile in the presence of MgCl₂ salt, as described for Mg(II)Pc-**1**. The detailed synthetic procedures and characterization data are given in the ESI.

Our first attempt to prepare the bulky version of the Ru(II)-Pc (**TT256**) was based on the synthetic route developed for **TT35** (*vide supra*). Unfortunately, during the synthetic sequence it was found that phthalocyanines with bulky substituents are more sensitive to standard ruthenium-metallation conditions (*i.e.*, heating at 220 °C for 24 h). Then, we envisioned an alternative synthetic route which consisted of preparing the corresponding Ru(II)PcCO intermediate under milder reaction conditions (*i.e.*, heating at 180 °C for 6 h) and subsequent carbonyl removal of the ruthenium(II) phthalocyaninato with concomitant substitution with 4-methylpyridine axial ligands. With the goal of maximum convergence, the ruthenium-metallation reaction was carried out on free-base Pc **11** that incorporates the carboxylic acid function protected as methyl ester. Thus, upon protection of the carboxyl group in **TT255** using methyl iodide in the presence of K₂CO₃ in acetone, the corresponding phthalocyanine **11** was obtained in almost quantitative yield after purification by column chromatography (Scheme 3). Subsequently, compound **11** was reacted with Ru₃(CO)₁₂ in refluxing *o*-DCB for 6 h to give the Ru(II)PcCO **12** in 80% yield. Ru(II)Pc **13** was obtained smoothly by heating Ru(II)Pc **12** in the presence of an excess of 4-methylpyridine and decarbonylation reagent (CH₃)₃NO in CHCl₃.^[18] Finally, the methyl ester group in Ru(II)Pc **13** was cleaved under very mild conditions to afford the target Pc **TT256** in 75% yield. Interestingly, this new approach implied the synthesis of magnesium (**TT254**) and free-base (**TT255**) Pcs, which were also incorporated in DSSC devices.



Scheme 3. Synthesis of **TT254**, **TT255** and **TT256**: (i) IBX, DMSO/acetone, rt, 24 h (92%); (ii) NaClO₂, NH₂SO₃H, THF/H₂O, 0 °C, 1 h (78%); (iii) CF₃COOH, CH₂Cl₂, rt, 3 h (82%); (iv) CH₃I, K₂CO₃, acetone, rt, 24 h (89%); (v) Ru₃CO₁₂, *o*-DCB, 180 °C, 6 h (84%); (vi) 4-methylpyridine, (CH₃)₃NO, CHCl₃, 70 °C, 4 h (86%); (vii) LiOH, THF/CH₃OH/H₂O, rt, 24 h (75%).

Optical Characterization

The molecular structures of all new Pcs were confirmed by IR, UV-Visible, and NMR spectroscopies and mass spectrometry (ESI or MALDI-TOF techniques).

As mentioned above, the absorption and emission properties of Pcs can be strongly affected by the nature of the metal ion present in the central cavity of the macrocycle. Figures 2a and 2b show the UV-Visible spectra of the tri-*tert*-butyl

substituted Pcs **TT1**, **TT28**, **TT33**, **TT35** and their bulky analogues **TT254**, **TT255**, **TT256** and **PcS18** respectively, in THF solution. Typical absorption features of phthalocyanines are observed for free-base, Zn(II), and Mg(II) Pcs: a strong Q-band in the lower energy region and a less intense B-band in the higher energy region. As expected, bulky-substituted Pcs exhibit a sharper Q-band absorption because of their very low aggregation behavior in solution. The nature of the metal center strongly affects the absorption properties of each Pc. For example, derivatives **TT28** and **TT255** exhibit a split Q-band characteristic of metal-free Pcs. Absorption bands of Ru(II) derivatives **TT35** and **TT256** are blue-shifted compared to Zn(II), Mg(II), and free-base Pcs, and interestingly, their Q-band exhibit broader absorption but with a lower extinction coefficient. In addition, Ru(II) Pcs present an extra band located around 380 nm that is attributed to a metal-to-ligand charge transfer ($d \rightarrow \pi^*$).

Electrochemistry

The electrochemical behavior of all the Pcs was investigated by cyclic voltammetry (CV) and square wave voltammetry (SWV) in THF solution. The half-wave redox potential values *versus* Fc⁺/Fc are summarized in Table 1. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of Pcs were determined from the redox potentials of electrochemical measurements. It is well-known that the electrochemical properties of Pc derivatives can be tuned by either varying the metal center or the type and position of the substituents on the macrocycle ring.^[19] In the tri-*tert*-butyl series, the electrochemical experiments revealed for **TT1** ($E_{1/2}(\text{ox}^1) = +0.26$ V and $E_{1/2}(\text{red}^1) = -1.62$ V) and **TT33** ($E_{1/2}(\text{ox}^1) = +0.25$ V and $E_{1/2}(\text{red}^1) = -1.61$ V) similar electrochemical properties, which implicates that the presence of Zn(II) or Mg(II)

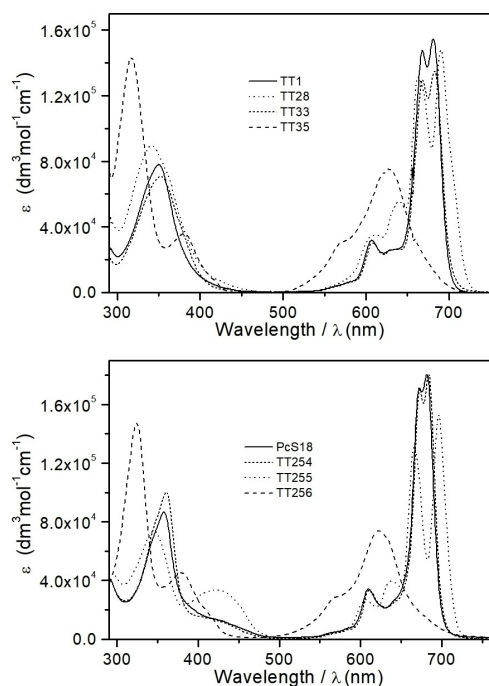


Figure 2. UV/vis spectra of (above) **TT1** (solid), **TT28** (dot), **TT33** (short dash), **TT35** (dash) and (below) **PcS18** (solid), **TT254** (short dash), **TT255** (dot), and **TT256** (dash) in THF solution.

Table 1. Electrochemical data for Pcs.^[a]

Pcs	Oxidation $E_{1/2}$ [V]	Reduction $E_{1/2}$ [V]	$E_{\text{HOMO}}^{[b]}$ [eV]	$E_{\text{LUMO}}^{[c]}$ [eV]
TT1	+0.26	−1.62	−5.36	−3.48
TT33	+0.25	−1.61	−5.35	−3.49
TT28	+0.30	−1.18	−5.40	−3.92
TT35	+0.26	−1.90	−5.36	−3.20
PcS18	+0.34	−1.43	−5.44	−3.67
TT254	+0.26	−1.61	−5.36	−3.49
TT255	+0.53	−1.22	−5.63	−3.88
TT256	+0.27	−1.94	−5.37	−3.16

[a] Electrochemical measurements were performed at room temperature using a three-electrode cell in argon-degassed THF solution containing 0.1 M TBAPF₆ as supporting electrolyte. A glassy carbon working electrode, a Pt wire counter electrode and an Ag/AgNO₃ reference electrode were used. Ferrocene (Fc) was used as external reference. [b] E_{HOMO} was calc. as: $E_{\text{HOMO}} = -(E_{\text{onset, ox}}^1 \text{ vs Fc/Fc}^+ + 5.1)$ (eV). [c] E_{LUMO} was calc. as: $E_{\text{LUMO}} = -E_{\text{onset, red}}^1 \text{ vs Fc/Fc}^+ + 5.1)$ (eV).

as metal center does not have any influence over the HOMO-LUMO gap. In the case of TT28 ($E_{1/2}(\text{ox}^1) = +0.30$ V and $E_{1/2}(\text{red}^1) = -1.18$ V), both the first oxidation and first reduction potentials are positively shifted compared to that of TT1.

It is worth noting that the significant negative shift of the first reduction of TT28 *versus* TT1 by 0.44 V indicates that free-base Pcs have a stronger acceptor character than Zn(II) derivatives. The effect of substituents species was examined by comparing the electrochemistry of metal-free Pcs (TT28 and TT255) to rule out any electronic effect due to the presence of the metal center. The substitution of three *tert*-butyl groups by six 2,6-diisopropylphenoxy substituents at the peripheral positions of the Pc macrocycle induces a remarkable positive shift for the first oxidation (TT28 ($E_{1/2}(\text{ox}^1) = +0.30$ V *versus* TT255 ($E_{1/2}(\text{ox}^1) = +0.53$ V) and a very slight negative shift for the first reduction (TT28 $E_{1/2}(\text{red}^1) = -1.18$ V *versus* TT255 $E_{1/2}(\text{red}^1) = -1.22$ V), resulting in a significant increased HOMO-LUMO gap of the compounds. For Zn(II)Pcs, a similar but less pronounced positive shift on the first oxidation was observed (TT1 ($E_{1/2}(\text{ox}^1) = +0.26$ V *versus* PcS18 ($E_{1/2}(\text{ox}^1) = +0.34$ V) and, in contrast, a positive shift on the first reduction was observed (TT1 $E_{1/2}(\text{red}^1) = -1.62$ V *versus* PcS18 ($E_{1/2}(\text{red}^1) = -1.43$ V). It is noteworthy that in the case of Ru(II) and Mg(II) Pcs, both the first oxidation and the first reduction remain almost unchanged independently of the peripheral substituent, *i.e.*, TT35 ($E_{1/2}(\text{ox}^1) = +0.26$ V and $E_{1/2}(\text{red}^1) = -1.90$ V) and TT256 ($E_{1/2}(\text{ox}^1) = +0.27$ V and $E_{1/2}(\text{red}^1) = -1.94$ V).

Photovoltaic Studies

The Pc sensitizers were tested in DSSCs on [6 + 4] μm thick TiO₂-films, which consist of a 6 μm thick active layer and an additional 4 μm thick scattering layer. For the preparation of the devices, the TiO₂ photoanodes were immersed in a 5 μM solution of Pc in THF for 16 h. The electrolyte used in this study

is composed of 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPImI), 0.1 M lithium iodine (LiI), 0.05 M iodine (I₂) and 0.5 M *tert*-butylpyridine (TBP) in acetonitrile. The photovoltaic performances of the DSSC devices made with TT1, TT28, TT33, TT35, TT254, TT255, TT256 and PcS18 dyes were measured under global AM 1.5 simulated solar conditions (Figure 3). Table 2 lists the photovoltaic data obtained for the DSSC devices, namely the short-circuit photocurrent density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and power conversion efficiency (PCE). The DSSCs based on Zn(II)Pcs were found to exhibit the highest PCEs independently of the nature of the peripheral substituents. It is worth noting that two benchmark dyes such as TT1 and PcS18 are tested and compared for the first time under the same conditions. The TT1 cell showed a J_{sc} of 9.1 mA cm^{-2} , a V_{oc} of 0.55 V, and a FF of 0.73, giving an overall PCE of 3.6% (Figure 3a,b and Table 2) whereas the Pc18 cell showed a J_{sc} of 11.4 mA cm^{-2} , a V_{oc} of 0.62 V, and a FF of 0.70, giving an overall PCE of 4.9% (Figure 3c,d and Table 2). It is well-established that prevention of aggregation plays an important role in the efficiency of DSSCs based on Pc dyes and indeed the presence of bulky substituents in PcS18 accounts for the improvement in device performance compared to TT1.

The same trend in efficiency (*tert*-butyl *versus* bulky substitution) but with a more pronounced effect was observed for the Mg(II)Pc derivatives, with an impressive two-fold increase in the PCE from 1.69% to 3.43% for TT33 and TT255, respectively. As well, the presence of bulky substituents in TT255 accounts for the reduced aggregation and hence improvement in device performance compared to TT33. Nevertheless, these values are almost twice less than those obtained with their Zn(II)-Pc analogues TT1 (3.63%) and PcS18 (4.95%), respectively. The main notable difference in the individual photovoltaic parameters between Zn(II) and Mg(II) Pc-cells is essentially a significant decrease in the J_{sc} values by *ca.* 50% and 20%. This can be appreciated in their respective IPCE spectra (Figure 3a,c), which are mostly identical in shape but with constantly lower IPCE values for Mg(II) than for Zn(II), especially in the Q-band region where these differences reached more than 10–20%. Given that these Pcs display same geometry, and similar optical and electrochemical properties,

Table 2. Photovoltaic performances of the Pc-based DSSCs.^[a]

Pcs	V_{oc} [mV]	J_{sc} [mA cm^{-2}]	FF	PCE [%]
TT1	548	9.07	0.73	3.63
TT33	521	4.71	0.69	1.69
TT28	481	1.91	0.71	0.65
TT35	427	2.88	0.62	0.76
PcS18	621	11.40	0.70	4.95
TT254	567	8.49	0.71	3.43
TT255	463	1.07	0.70	0.35
TT256	427	0.93	0.57	0.23

[a] Dye-uptake solution: 5 μM in THF; dipping time: 24 h; electrolyte composition: 0.05 M I₂, 0.1 M LiI, 0.6 M DMPImI, 0.5 M TBP in AcCN; TiO₂ film: 6 μm transparent layer with 4 μm scattering layer.

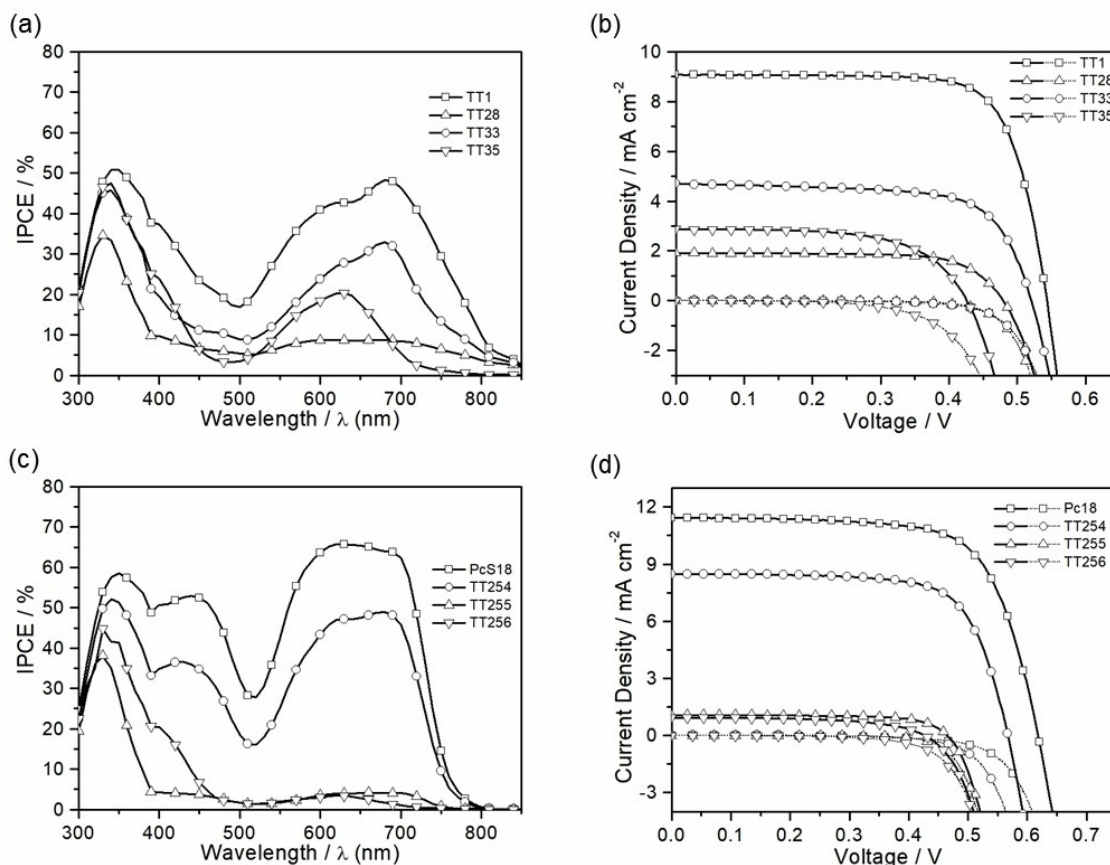


Figure 3. IPCE spectra (a) and photocurrent-voltage curves (b) for DSSCs based on TT1 (\square), TT28 (\triangle), TT33 (\circ), TT35 (∇) and IPCE spectra (c) and photocurrent-voltage curves (d) for DSSCs based on Pc18 (\square), TT255 (\triangle), TT254 (\circ), TT35 (∇).

one would expect no important differences in electron-injection and dye-regeneration efficiencies, dye-loading (packing) and light-harvesting capabilities of the sensitized films. Therefore, we suggest that faster charge-recombination dye-TiO₂ should occur in Mg(II)Pc-DSSCs with respect to Zn(II) ones, which should be responsible of the lower IPCE response (hence lower J_{SC} and PCE).

Turning to the free-base Pcs, the PCE values of the devices made with TT58 and TT255 are one order of magnitude lower than those obtained with their respective Zn(II)-Pc benchmarks TT1 and PcS18. Their IPCE spectra shows maximum values of only *ca.* 5–10% in the Q-band region, in sharp contrast with those reached by the Zn(II)-analogues (over 50–65%). The low PCEs obtained with these sensitizers can be explained by the mismatch between their LUMO level and the conduction band of the TiO₂, which results in an insufficient driving force to ensure an efficient electron-injection Dye \rightarrow TiO₂. The LUMO energy level of both TT255 and TT28 are positioned around -3.9 eV, which is 0.15 eV above the energy level of the conducting band of the TiO₂ oxide (around -4.05 eV). Therefore, it seems that the LUMO energy levels of the free-base Pcs are not high enough in energy to achieve an efficient electron-injection. Regarding the Ru(II)Pc derivatives, the TT35 and TT256 cells also gave poor efficiencies (0.76% and 0.25%,

respectively) despite having in this case adequate HOMO-LUMO energy levels. In our previous study, we showed that TT35 is characterized by a rapid intersystem crossing to a long-lived triplet state, as well as higher injection efficiency than TT1, but gave a lower overall efficiency.^[17] The main explanation was ascribed to the lower light-harvesting capabilities of the Ru(II)-Pc film. Hence, this is not surprising that the bulky dye TT256 gave lower efficiency than the tri-*tert*-butyl analogue TT35, which points out that aggregation is indeed not the issue for these Ru(II)Pc sensitizers. Instead, the bulkier groups in TT256 just reduce the dye-loading and hence the light-harvesting properties of the Pc-film, which should mainly account for the lower PCE.

Conclusions

Herein, we have reported on the synthesis, photophysical and electrochemical characterization of two series of free-base (H₂Pcs) and metallo phthalocyanines (MPcs, with M = Zn(II), Mg(II) and Ru(II)), and their photovoltaic performances in DSSCs. The novel Pc-sensitizers present the carboxyl anchoring group directly attached to the macrocycle and have either *tert*-butyl or 2,6-diisopropylphenoxy groups as peripheral substituents. In-

dependently of the nature of the peripheral groups, the trend in photovoltaic performances systematically followed the order $\text{Zn(II)Pc} > \text{Mg(II)Pc} \gg \text{H}_2\text{Pc} \approx \text{Ru(II)Pc}$. The synthetic strategies developed in this work will pave the way for the exploration of novel Pc-sensitizers with potential applications in molecular photovoltaics.

Experimental Section

Synthetic procedures. Additional experimental procedures and synthesis and characterization of novel compounds (MS, NMR and UV/Vis spectra) are provided in the Supporting Information.

2(3),9(10),16(17)-tri-*tert*-butyl-23-(carboxy)phthalocyaninato magnesium(II) (TT33): To a stirred solution of **MgPc 2** (100 mg, 0.136 mmol) in THF (25 ml) a solution of sulfamic acid (40 mg, 0.412 mmol) in Milli-Q-grade deionized water (4 ml) was added. Then, the mixture was cooled to 0 °C and a solution of NaClO_2 (38 mg, 0.336 mmol) in Milli-Q-grade deionized water (4 ml) was added dropwise. The reaction mixture was vigorously stirred at 0 °C for 30 min, then the mixture was poured into aqueous HCl (1 M) and extracted with EtOAc. The organic phase was washed with brine, dried over anhydrous MgSO_4 , and concentrated under vacuum. The desired compound **TT33** was further purified by column chromatography on silica gel using $\text{CHCl}_3/\text{MeOH}$ (100:1) as eluent to give the pure compound as a dark blue solid (75 mg, Yield: 74%). ^1H NMR (300 MHz, THF-d_8): δ (ppm) = 10.12 (br s, 1H), 9.5 (br m, 7H), 8.8 (br s, 1H), 8.3 (br s, 3H), 1.8 (m, 27H); UV/Vis (THF): λ_{max} (nm) (ϵ , $\times 10^3 \text{ M}^{-1}\text{cm}^{-1}$) = 353 (60), 600 (sh), 668 (125), 683 nm (135); FT-IR (KBr): ν (cm^{-1}) = 3416, 2957, 2904, 2867, 1697, 1613, 1486, 1393, 1364, 1325, 1282, 1256, 1200, 1149, 1080, 1149, 1080, 1046, 923, 832, 752, 692; HRMS (MALDI-TOF, DITRANOL): calc. for $\text{C}_{45}\text{H}_{40}\text{MgN}_8\text{O}_2$: $[\text{M}]^+$: m/z : 748.3119, found 748.3104.

2(3),9(10),16(17)-tri-*tert*-butyl-23-(carboxy)phthalocyanine (TT28): Compound **TT33** (100 mg, 0.135 mmol) was dissolved in EtOAc (20 ml), then TFA (0.2 ml) was added, and the solution was stirred for 3 h. Dichloromethane (50 ml) was then added, and the solution was washed carefully with 5% NaHCO_3 and water. The organic phase was dried over Na_2SO_4 anhydrous, and the solvent was evaporated under vacuum. The residue was purified by reverse phase column chromatography employing $\text{THF}/\text{H}_2\text{O}$ (2:1) as eluent to give the desired compound **TT-28** (91 mg, Yield: 93%). ^1H NMR (300 MHz, THF-d_8): δ (ppm) = 9–7.7 (m, 12H), 1.8 (m, 27H), –3.8 (m, 2H, NH^{p}); UV/Vis (THF): λ_{max} (nm) (ϵ , $\times 10^3 \text{ M}^{-1}\text{cm}^{-1}$) = 341 (80), 601 (sh), 639 (38), 663 (130), 691 nm (148); FT-IR (KBr): ν (cm^{-1}) = 3442, 3291, 2956, 2905, 2867, 1688, 1615, 1482, 1417, 1393, 1364, 1332, 1317, 1282, 1258, 1241, 1200, 1089, 1014, 925, 830, 747, 691; HRMS (MALDI-TOF, DITRANOL): calc. for $\text{C}_{45}\text{H}_{42}\text{N}_8\text{O}_2$: $[\text{M}]^+$: m/z : 726.3425, found 726.3446.

Bis(4-methylpyridine)-2(3),9(10),16(17)-tri-*tert*-butyl-23-(carboxy)phthalocyaninato ruthenium(II) (TT35): To a stirred solution of **RuPc 8** (0.04 mmol) in THF (10 ml) a solution of sulfamic acid (0.12 mmol in 2 ml of Milli-Q-grade deionized water) was added. Then, the mixture was cooled to 0 °C and a solution of NaClO_2 (0.1 mmol in 1 ml of Milli-Q-grade deionized water) was added in a few portions. The reaction mixture was vigorously stirred at 0 °C for 30 min, then the mixture was poured into aqueous HCl (1 M) and extracted with EtOAc. The organic phase was washed with brine, dried over anhydrous MgSO_4 and concentrated under vacuum. The desired compound **TT35** was further purified by column chromatography on silica gel using $\text{CHCl}_3/\text{MeOH}$ (100:1) as eluent to give the pure compound as a dark blue solid (26 mg, Yield: 64%). ^1H NMR (300 MHz, THF-d_8): δ (ppm) = 9.6 (m, 1H^a), 9.1 (m, 7H), 8.4 (m, 1H), 8.0 (m, 3H), 5.42 (d, J = 6.4 Hz, 4H), 2.25 (d, J =

6.4 Hz, 4H), 1.7 (m, 27H), 1.14 (s, 6H); UV/Vis(THF): λ_{max} (nm) (ϵ , $\times 10^3 \text{ M}^{-1}\text{cm}^{-1}$) = 317 (143), 381 (35), 627 nm (76); FT-IR (KBr): ν (cm^{-1}) = 3422, 2956, 2868, 1684 (C=O), 1614, 1484, 1431, 1391, 1362, 1314, 1281, 1231, 1153, 1120, 1051, 861, 810, 766, 755; HR-ESI (methanol + 1% TFA) calcd for $\text{C}_{57}\text{H}_{55}\text{N}_{10}\text{O}_2\text{Ru}$: $[\text{M} + \text{H}]^+$: m/z : 1013.3563, found 1013.3526.

2,3,9,10,16,17-hexa-2,6-diisopropylphenoxy-23-(carboxy) phthalocyaninato magnesium(II) (TT254): To a stirred solution of **Mg(II)Pc 10** (140 mg, 0.086 mmol) in THF (5 ml) a solution of sulfamic acid (49 mg, 0.50 mmol) in Milli-Q-grade deionized water (2 ml) was added. Then, the mixture was cooled to 0 °C and a solution of NaClO_2 (12 mg, 0.138 mmol) in Milli-Q-grade deionized water (1 ml) was added dropwise. The reaction mixture was vigorously stirred at 0 °C for 1 h, then the mixture was poured into aqueous HCl (1 M) and extracted with CH_2Cl_2 . The organic phase was washed with brine, dried over anhydrous MgSO_4 , and concentrated under vacuum. The desired compound **TT254** was further purified by column chromatography on silica gel using $\text{CHCl}_3/\text{MeOH}$ (20:1) as eluent to give the pure compound as a green solid (110 mg, Yield: 78%). ^1H -NMR (300 MHz, THF-d_8): δ (ppm) = 9.84 (br s, 1H), 9.24 (d, J = 7.9 Hz, 1H), 8.70 (br s, 1H), 8.49 (s, 1H), 8.43 (s, 1H), 8.25 (s, 1H), 8.24 (s, 1H), 8.19 (s, 2H), 7.67 (m, 4H), 7.58 (m, 14H), 3.50 (m, 12H), 1.39 (m, 72 H); UV/vis (THF): UV/Vis(THF): λ_{max} (nm) (ϵ , $\times 10^3 \text{ M}^{-1}\text{cm}^{-1}$) = 360 (100), 611 (33), 673 (170), 684 nm (180); FT-IR (KBr): ν (cm^{-1}) = 3376, 2962, 2868, 1715, 1685, 1608, 1606, 1454, 1439, 1399, 1361, 1340, 1329, 1274, 1221, 1189, 1145, 1094, 1075, 1061, 1045, 960, 936, 895, 793, 753, 724; HR-MS (MALDI-TOF, DCTB): calc. for $\text{C}_{105}\text{H}_{112}\text{MgN}_8\text{O}_8$: $[\text{M}]^+$: m/z : 1636.8448, found 1636.8455.

2,3,9,10,16,17-hexa-2,6-diisopropylphenoxy-23-(carboxy) phthalocyanine (TT255): Compound **TT254** (130 mg, 0.079 mmol) was dissolved in CH_2Cl_2 (12 ml), then TFA (0.5 ml) was added, and the solution was stirred for 3 h. Dichloromethane (50 ml) was added, and the solution was washed carefully with 5% NaHCO_3 in water. The organic phase was dried over MgSO_4 anhydrous, and the solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel using $\text{CHCl}_3/\text{MeOH}$ (15:1) as eluent to give **TT255** as a green solid (106 mg, Yield: 82%). ^1H -NMR (300 MHz, CDCl_3): δ (ppm) = 9.97 (s, 1H), 9.34 (d, J = 7.9 Hz, 1H), 8.83 (dd, J = 7.9, 1.3 Hz, 1H), 8.57 (s, 1H), 8.52 (s, 1H), 8.34 (s, 1H), 8.32 (s, 1H), 8.10 (s, 2H), 7.59 (m, 6H), 7.50 (m, 12H), 3.47 (m, 12H), 1.39 (m, 72 H), –0.62 (s, 2H); UV/vis (THF): λ_{max} (nm) (ϵ , $\times 10^3 \text{ M}^{-1}\text{cm}^{-1}$) = 345 (68), 422 (30), 607 (sh), 638 (sh), 666 (122), 695 nm (142); IR (KBr): ν (cm^{-1}) = 3391, 2959, 2770, 1714, 1685, 1608, 1463, 1444, 1398, 1362, 1345, 1328, 1273, 1226, 1175, 1110, 1091, 1060, 1017, 959, 879, 850, 793, 750, 711; HR-MS (MALDI-TOF, DCTB): calc. for $\text{C}_{105}\text{H}_{114}\text{N}_8\text{O}_8$: $[\text{M}]^+$: m/z : 1614.8754, found 1614.8752.

Bis(4-methylpyridine)-2,3,9,10,16,17-hexa-2,6-diisopropylphenoxy-23-(carboxy) phthalocyaninato ruthenium(II) (TT256): Compound **Ru(II)Pc 13** (50 mg, 0.026 mmol) was dissolved in a mixture of THF (3 ml) and Methanol (1 ml), then a solution of LiOH (3 mg, 0.12 mmol) in water (0.5 ml) was added to the reaction mixture, which was stirred at room temperature for 24 h. The solved mixture was evaporated, and the crude was dissolved in CH_2Cl_2 (100 ml), then the solution was washed with HCl 1 M (20 ml) and water (50 ml). The organic phase was dried over MgSO_4 anhydrous, and the solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel using $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (15:1) as eluent to give **TT256** as a blue solid (37 mg, Yield: 75%). ^1H -NMR (300 MHz, Acetone- d_6): δ (ppm) = 9.43 (s, 1H), 8.82 (d, J = 7.9 Hz, 1H), 8.41 (dd, J = 7.9, 1.5 Hz, 1H), 8.08 (s, 1H), 8.04 (s, 1H), 7.87 (s, 2H), 7.85 (s, 1H), 7.83 (s, 1H), 7.70 (m, 4H), 7.60 (m, 8H), 7.53 (m, 6H), 5.20 (d, J = 6.8 Hz, 4H), 3.52 (m, 12H), 2.21 (d, J = 6.8 Hz, 4H), 1.34 (m, 72 H), 1.14 (s, 6H); UV/vis (THF): λ_{max} (nm) (ϵ , $\times 10^3 \text{ M}^{-1}\text{cm}^{-1}$) = 324 (148), 379 (45), 622 nm (74); IR (KBr): ν (cm^{-1}) =

3386, 2959, 2880, 1718, 1608, 1491, 1475, 1456, 1438, 1407, 1362, 1330, 1269, 1185, 1152, 1110, 1093, 1060, 1035, 960, 937, 906, 877, 855, 794, 779, 753, 724; HR-ESI (methanol+1% TFA) calcd for $C_{117}H_{126}N_{10}O_8Ru$: $[M+H]^+$: m/z : 1901.8876, found 1901.8846.

Acknowledgements

T.T. acknowledges financial support from the Spanish MCIN/AEI/10.13039/501100011033 (PID2020-116490GB-I00 and TED2021-131255B-C43) and the Comunidad de Madrid and the Spanish State through the Recovery, Transformation and Resilience Plan ["Materiales Disruptivos Bidimensionales (2D)" (MAD2D-CM) (UAM1)-MRR Materiales Avanzados], and the European Union through the Next Generation EU funds. IMDEA Nanociencia acknowledges support from the "Severo Ochoa" Programme for Centres of Excellence in R&D (MINECO, Grant SEV2016-0686).

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Phthalocyanine · Dye sensitized solar cells · Molecular Photovoltaics

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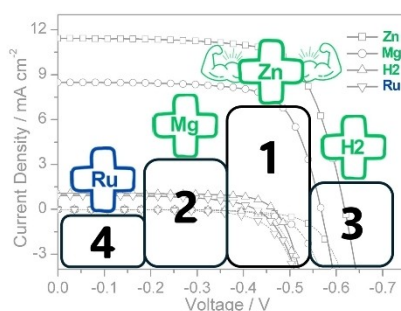
Manuscript received: February 2, 2024

Accepted manuscript online: April 29, 2024

Version of record online: ■■■

RESEARCH ARTICLE

A series of metallo-(Zn(II), Mg(II) and Ru(II)) and free-base phthalocyanines (Pcs) with a carboxyl anchoring group and either *tert*-butyl or bulky 2,6-diisopropylphenoxy peripheral substituents were synthesized and tested as sensitizer in DSSCs to shed light on the role of central metals in photovoltaic performance. Regardless of peripheral substitution, the trend of photovoltaic efficiencies followed the order Zn(II)Pc > Mg(II)Pc \gg H₂Pc \approx Ru(II)Pc.



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Exploring the Role of Central Metals in Bulky Phthalocyanines for Dye-Sensitized Solar Cells

