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## Efficient Synthesis and Microwave-Assisted Sonogashira Reactions of Triflate-Substituted Porphyrin

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Nicola Demitri,<sup>[d]</sup> Michele Maggini,<sup>\*[a]</sup> and Luka Đorđević<sup>\*[a]</sup>Dedicated to Prof. Maurizio Prato on the occasion of his 70<sup>th</sup> birthday

Porphyrins that bear halogens at the *meso*-aryl positions are useful building blocks for the preparation of light-harvesting arrays and materials through cross-coupling procedures. Despite the wide use of such intermediates, their scale-up and purification are usually hampered by tedious chromatographic separations because of the statistical nature of the synthetic protocol and the similar polarity of the different products. Here, we propose the use of porphyrins bearing a triflatophenyl group as alternative starting materials for palladium cross-coupling reactions. In particular, purification of the zinc 5,10,15-triaryl-20-(4-triflatophenyl)porphyrin (ZnP-OTf) model compound by column chromatography proved to be much easier compared to porphyrin analogues that carry halogen substitu-

ents. This is the result of the increased polarity of compounds functionalized by highly polar triflate groups if compared to those substituted by halogens. To show the value of the triflatophenylporphyrin model compound in cross-coupling reactions, we developed a microwave-assisted Sonogashira protocol that quantitatively converts the ZnP-OTf to the corresponding alkynylporphyrin, in relatively short reaction times. Finally, we showed that the proposed ZnP-OTf building block can be conveniently converted into an alkynyl-linked molecular wire to bridge the zinc porphyrin donor with the [60]fullerene acceptor in a molecular dyad. The prepared dyad showed efficient photoinduced charge separation from singlet ZnP excited state to [60]fullerene in a polar solvent.

## Introduction

Halogenated porphyrins are central building blocks in tetrapyrrole chemistry because their cross-coupling reactions allow the introduction of various substituents and functionalities, making thus halogenated porphyrins essential for the construction of molecular and supramolecular structures that range from the nanoscale to the mesoscale.<sup>[1]</sup> Halophenylporphyrins, carrying either iodine or bromine groups, have been particularly useful for various palladium cross-coupling methods that include Sonogashira coupling,<sup>[2]</sup> Suzuki–Miyaura coupling,<sup>[3]</sup> Migita–Kosugi–Stille coupling,<sup>[4]</sup> and Hirao coupling,<sup>[5]</sup> as well as Mizoroki–Heck reaction,<sup>[6]</sup> and Buchwald–Hartwig amination.<sup>[7]</sup> Especially the Sonogashira methodology has been successfully applied to integrate *meso*-halophenyl tetrapyrrolic compounds into e.g. light-harvesting multichromophore arrays,<sup>[2e,8]</sup> nanorotors,<sup>[9]</sup> and molecular quantum information systems.<sup>[10]</sup>

However, 5,10,15-triaryl-20-(iodophenyl)porphyrins (ZnP-I, Figure 1a) prepared by a mixed aldehyde condensation method usually yield a mixture of porphyrins. The isolation of the desired porphyrin (A<sub>3</sub>B, with one iodophenyl substituent) by column chromatography is notoriously challenging, owing to very similar polarities between aryl and halophenyl groups. We reasoned that replacing the iodine (or bromine) substituents with another moiety that has similar reactivity but very different polarity, such as the trifluoromethanesulfonyl (triflate, OTf) group, would greatly simplify the purification of A<sub>3</sub>B porphyrin building blocks. While the triflate group has not been exploited to facilitate the purification of A<sub>3</sub>B porphyrins, its feasibility as

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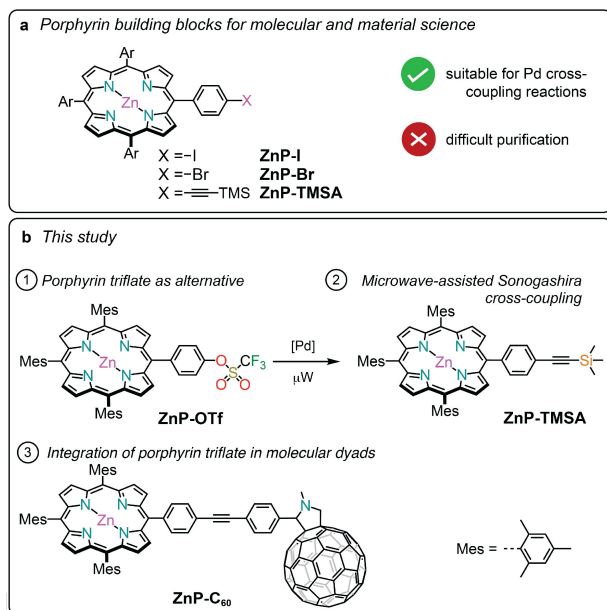
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**Figure 1.** Chemical structures of functionalized porphyrins discussed in this work.

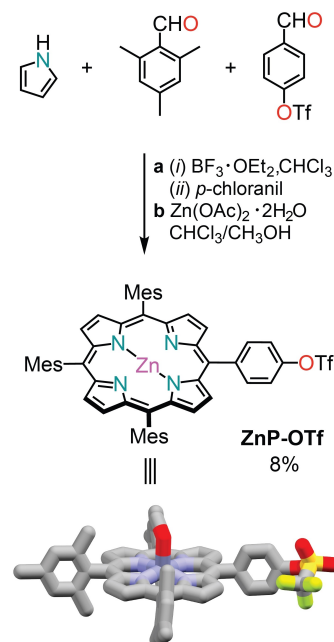
partner in palladium cross coupling reactions has been reported in porphyrin chemistry. For example, porphyrins bearing multiple peripheral triflate groups have been employed in Suzuki,<sup>[11]</sup> Stille<sup>[12]</sup> and Sonogashira<sup>[13]</sup> cross-coupling reactions. While A<sub>4</sub> and A<sub>2</sub>B<sub>2</sub> porphyrins, bearing peripheral triflates, have been prepared through condensation of pyrrole (or dipyrromethene) and 4-formylaryl trifluoromethanesulfonate, in the case of A<sub>3</sub>B porphyrins the installation of triflate groups is usually performed through multistep procedures.<sup>[11a,12]</sup>

In this research article, we propose that the zinc(II) 5,10,15-trimesityl-20-(4-triflatophenyl)porphyrin (ZnP-OTf, Figure 1b) could be used as an alternative to the ZnP-I and to the ethynylphenylporphyrin (ZnP-TMSA, Figure 1b) for the preparation of light-harvesting arrays. While having been extensively used, the latter two need, after the mixed aldehyde synthesis, tedious and time-consuming column chromatography for their purification (usually hexane/dichloromethane 10:1 v/v). In addition to the synthesis and easy purification of the ZnP-OTf, we developed a microwave-assisted Sonogashira cross-coupling that allows to readily obtain ZnP-TMSA. Finally, to highlight the function of the ZnP-OTf, we synthesized a donor-acceptor dyad consisting of a ZnP covalently linked to [60]fullerene through an acetylene spacer (ZnP-C<sub>60</sub>, Figure 1b). As expected, the dyad showed emission quenching of the porphyrin likely ascribable to photoinduced intramolecular charge transfer, as supported by a Rehm–Weller analysis.

## Results and Discussion

### Synthesis of ZnP-OTf

First, 4-formylphenyl trifluoromethanesulfonate was prepared by reacting 4-hydroxybenzaldehyde with triflic anhydride, in the presence of pyridine, giving the desired product in an isolated yield of 85%. Then, the A<sub>3</sub>B ZnP-OTf porphyrin was prepared by the mixed aldehyde condensation with pyrrole under Lindsey conditions<sup>[14]</sup> in a two-step one-pot route, followed by metalation with a zinc salt (Figure 2). In the first step, condensation of mesitaldehyde, 4-formylphenyl trifluoromethanesulfonate and pyrrole, under BF<sub>3</sub>·OEt<sub>2</sub> catalysis in degassed chloroform, followed by oxidation with *p*-chloranil, gave the expected A<sub>4</sub>, A<sub>3</sub>B, A<sub>2</sub>B<sub>2</sub>, and AB<sub>3</sub> porphyrins mixture. The second step was the metalation of the porphyrins with Zn(OAc)<sub>2</sub> in a chloroform/methanol mixture. The zinc porphyrins mixture was then separated by column chromatography, taking advantage of the increased polarity of the triflate group, compared to that of the iodine or alkynyl substituents in ZnP-I and ZnP-TMSA respectively. For example, while iodophenyl and alkynylphenylporphyrins are usually separated with a mixture of hexane and dichloromethane 9:1 v/v, the ZnP-OTf could easily be isolated in a yield of 8% with a mixture of hexane-ethyl acetate 95:5 v/v (Supporting Information, Figures S15–S16). This yield is in line with those usually obtained by the mixed aldehyde condensation approach,<sup>[14]</sup> demonstrating that the triflate substituent does not negatively influence the yield of monosubstituted porphyrin. In addition to NMR spectrometry and high-resolution mass spectrometry, ZnP-OTf was unambiguously characterized by single-crystal XRD (Figure 2).



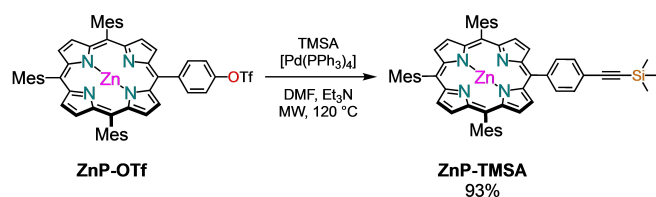
**Figure 2.** Synthetic route for the preparation of ZnP-OTf by the acid-catalyzed mixed aldehyde approach and its single-crystal X-ray structure (with a methanol molecule coordinated to the Zn center; hydrogens are omitted for clarity).

## Microwave-assisted Sonogashira cross-coupling of ZnP-OTf

The relative ease of purification of **ZnP-OTf** led to exploration of the reactivity and further optimization of the palladium-catalyzed cross-coupling reactions of this building block. Given previous research that used halophenylporphyrins to prepare alkynyl-linked multichromophoric arrays, we chose a model Sonogashira cross-coupling reaction between **ZnP-OTf** and trimethylsilylacetylene (TMSA). Sonogashira<sup>[15]</sup> conditions for the transformation of **ZnP-I** into **ZnP-TMSA** were previously optimized by Lindsey and co-workers.<sup>[2a,16]</sup> However, the reaction required a high palladium loading (15 mol%) and the use of  $\text{AsPh}_3$  as ligand (115 mol%) to proceed in good yields (> 70%) and relatively short times (> 2 h), usually followed by multiple column or size-exclusion chromatographies to obtain **ZnP-TMSA** in pure form. In an effort to improve the coupling protocol, we applied a controlled microwave heating, which, at least in principle, should deliver high reaction yields in relatively short reaction times.<sup>[17]</sup>

We found that the reaction proceeded with the quantitative conversion of **ZnP-OTf** to **ZnP-TMSA** (Scheme 1) and excellent isolated yields (93%) under the following conditions: tetrakis(triphenylphosphine)palladium ( $[\text{Pd}(\text{PPh}_3)_4]$ , 10 mol%) as Pd(0) source, triphenylphosphine ( $\text{PPh}_3$ , 20 mol%) as ligand, and triethylamine ( $\text{Et}_3\text{N}$ ) as base under microwave controlled heating (120 °C) for 60 minutes. In particular, this protocol does not require a copper co-catalyst, which could undergo transmetalation with zinc porphyrins<sup>[18]</sup> or easily insert into the tetrapyrrole macrocycle when free-base porphyrins are used.<sup>[16]</sup> In addition to NMR spectroscopy and high-resolution mass spectrometry, the compound **ZnP-TMSA** was unambiguously characterized by single-crystal XRD (Figure S21).

During control experiments, we noticed that in the absence of either  $[\text{Pd}(\text{PPh}_3)_4]$  or  $\text{Et}_3\text{N}$ , the starting material did not react. Without  $\text{PPh}_3$ , the conversion of **ZnP-OTf** to **ZnP-TMSA** was incomplete and the yield was only 40%, probably due to the triflate anion not coordinating strongly with palladium after oxidative addition.<sup>[19]</sup> Microwave heating less than 60 min also leads to incomplete conversion of the starting **ZnP-OTf**. On the other hand, the use of  $\text{LiCl}$  in place of  $\text{PPh}_3$  (yield = 86%) or the substitution of  $[\text{Pd}(\text{PPh}_3)_4]$  with  $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$  (yield = 88%) did not notably affect the conversion of **ZnP-OTf** to **ZnP-TMSA**.



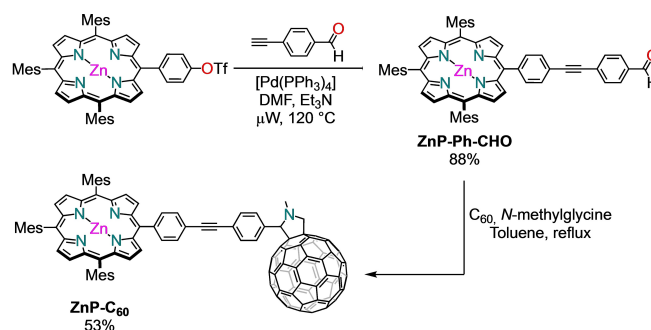
**Scheme 1.** Synthetic route for the preparation of **ZnP-TMSA** through microwave-assisted Sonogashira cross coupling (see Supporting Information for the single-crystal X-ray structure).

## Synthesis of a zinc porphyrin-[60]fullerene molecular wire

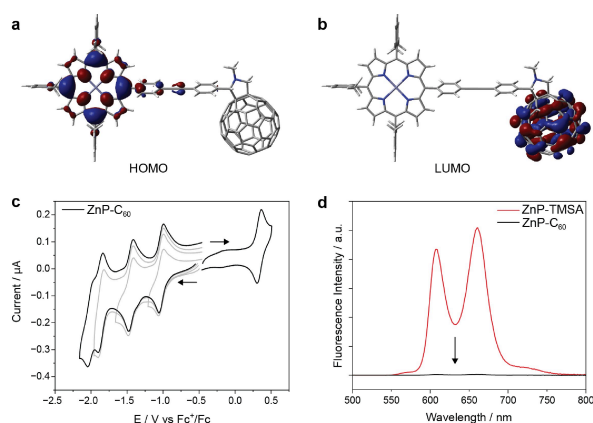
With a microwave-assisted Sonogashira cross-coupling protocol in hand, we also sought to convert **ZnP-OTf** into a model molecular wire, in which the phenylporphyrin is covalently linked to a fulleropyrrolidine through an ethynyl spacer. Among various multichromophoric arrays, porphyrins have been frequently used in combination with [60]fullerene to create donor-acceptor systems as artificial photosynthetic mimics.<sup>[20]</sup> Scheme 2 shows the synthesis of **ZnP-C<sub>60</sub>**, starting from **ZnP-OTf** and 4-ethynylbenzaldehyde<sup>[21]</sup> that, under the optimized Sonogashira coupling, gave the corresponding porphyrin benzaldehyde **ZnP-Ph-CHO**. This was used with *N*-methylglycine in a 1,3-dipolar cycloaddition with [60]fullerene<sup>[22]</sup> in toluene to obtain the desired dyad in a 53% isolated yield. **ZnP-C<sub>60</sub>** was unambiguously characterized by NMR and high-resolution mass spectrometry.

Using density functional theory (B3LYP functional with 6-31G\* and LanL2DZ basis sets) the dyad geometry was optimized and the frontier molecular orbitals of **ZnP-C<sub>60</sub>** were visualized (Figure 3a,b). Calculations showed that the HOMO is mostly localized on the porphyrin, with a minor contribution over the ethynylphenyl bridge. This suggests, to some extent, an overlap between the porphyrin and the  $\pi$ -orbitals of alkynyl spacer. The distribution of the electronic densities for the LUMO reveals the affinity for reduction of the fullerene.

The electrochemical properties of **ZnP-C<sub>60</sub>** were investigated by cyclic voltammetry in benzonitrile (0.5 mM, containing 0.1 M *n*-Bu<sub>4</sub>PF<sub>6</sub> as supporting electrolyte). Under cathodic scan, **ZnP-C<sub>60</sub>** showed four reversible one-electron waves at  $E_{1/2} = -1.03, -1.45, -1.87$  and  $-2.01$  V vs Fc<sup>+</sup>/Fc (Figure 3c and Table S3), attributed to  $\text{C}_{60}/\text{C}_{60}^{\bullet-}$ ,  $\text{C}_{60}^{\bullet-}/\text{C}_{60}^{2-}$ ,  $\text{ZnP}/\text{ZnP}^{\bullet-}$  and  $\text{C}_{60}^{2-}/\text{C}_{60}^{3\bullet-}$  redox processes, respectively.<sup>[23]</sup> Extending the scan toward more negative potentials, an additional quasi-reversible wave is observed at  $E_{1/2} = -2.31$  V, attributed to a further one-electron reduction on the porphyrin ring  $\text{ZnP}^{\bullet-}/\text{ZnP}^{2-}$  (Table S3 and Figure S20a). Under anodic scan, **ZnP-C<sub>60</sub>** shows two one-electron reversible processes at  $E_{1/2} = +0.34$  V and  $+0.75$  V, attributable to the  $\text{ZnP}^{\bullet+}/\text{ZnP}$  and  $\text{ZnP}^{2+}/\text{ZnP}^{\bullet+}$  couples from the stepwise oxidation of the porphyrin ring (Table S3 and Figure S20b; for the sake of simplicity, we represented only the



**Scheme 2.** Synthetic route for the preparation of the **ZnP-C<sub>60</sub>** donor-acceptor dyad. **ZnP-OTf** was subjected to microwave-assisted Sonogashira coupling to obtain porphyrin benzaldehyde **ZnP-Ph-CHO**, which was then used in a 1,3-dipolar cycloaddition reaction with *N*-methylglycine and [60]fullerene.



**Figure 3.** Computational, electrochemical and emission results for the ZnP-C<sub>60</sub> dyad. (a) frontier molecular orbitals (HOMO and LUMO) obtained from DFT calculations; (c) Cyclic voltammograms of ZnP-C<sub>60</sub> (0.5 mM in benzonitrile with 0.1 M *n*-Bu<sub>4</sub>PF<sub>6</sub> supporting electrolyte) under cathodic and anodic scans. Scan rate 0.1 Vs<sup>-1</sup>; (d) Photoluminescence emission spectra of ZnP-C<sub>60</sub> and ZnP-TMSA upon excitation at 429 nm in benzonitrile (the spectra are recorded at the same optical density (0.1) at the excitation wavelength).

first anodic process as shown in Figure 3c, since it is the one associated with the postulated photoinduced electron transfer in the dyad, *vide infra*). The attribution of the porphyrin based redox processes in ZnP-C<sub>60</sub> was corroborated by the cyclic voltammograms of ZnP-TMSA, where the cathodic processes were observed at  $E_{1/2} = -1.91$  V and  $-2.27$  V, while the anodic ones were observed at  $E = +0.37$  V and  $+0.79$  V (Table S3 and Figure S20).

Steady-state fluorescence spectra of ZnP-C<sub>60</sub> and ZnP-TMSA were measured in benzonitrile by exciting the Soret band where the compounds mostly absorb (Figure 3d). The emission of ZnP-C<sub>60</sub> ( $\Phi_{FL} = 0.34\%$ ) was very weak compared with that of ZnP-TMSA ( $\Phi_{FL} = 3.39\%$ ), showing almost complete quenching of the porphyrin excited singlet state (<sup>1</sup>ZnP\*) by [60]fullerene. The emission of ZnP-C<sub>60</sub> was observed only from the porphyrin at  $\lambda_{max} = 608$  and  $660$  nm, with no detectable [60]fullerene emission between 550–750 nm. For covalent ZnP-[60]fullerene dyads, it is known that the excitation of the porphyrin promotes a photoinduced electron transfer from the donor ZnP excited state to the [60]fullerene acceptor.<sup>[20]</sup> The standard free energy associated with such an electron transfer in ZnP-C<sub>60</sub> can be estimated using the Rehm–Weller equation:<sup>[24]</sup>  $\Delta G^\circ = E(\text{ZnP}/\text{ZnP}^{*+}) - E(\text{C}_{60}/\text{C}_{60}^{\bullet-}) - \Delta E_{00}$  where  $E(\text{ZnP}/\text{ZnP}^{*+})$  and  $E(\text{C}_{60}/\text{C}_{60}^{\bullet-})$  are the first oxidation potential of the donor and the first reduction potential of the acceptor, respectively, while  $\Delta E_{00}$  is the energy of the 0–0 transition between the ground state and the lowest excited state. Electrochemical data, together with the emission spectral signature, allowed us to estimate the driving force for electron transfer <sup>1</sup>[ZnP]\* → C<sub>60</sub> to be  $-0.68$  eV without considering correction for electrostatic effects. On this basis, the existence of a transient ZnP<sup>\*+</sup>–C<sub>60</sub><sup>•-</sup> charge separated (CS) state in our ZnP-C<sub>60</sub> dyad can be anticipated. Also, the molecular spacer between the donor and acceptor units would be in favor of stabilizing the CS state by placing the radical pair apart. Also, it is well established that porphyrin-[60]fullerene

dyads undergo efficient photoinduced charge separation from <sup>1</sup>ZnP\* to [60]fullerene in a polar solvent, such as benzonitrile.<sup>[20]</sup> For alkynyl-linked ZnP-[60]fullerene dyads (analogous to that reported here but with different aryl groups on the ZnP) it was determined, through time-resolved transient absorption spectroscopy, that the rates of charge separation, evolving from <sup>1</sup>ZnP\* to [60]fullerene ( $k_{ET(\text{CS})} = 3.0 \times 10^{10}$  s<sup>-1</sup>) were much larger than those for charge recombination in the ZnP<sup>\*+</sup>/C<sub>60</sub><sup>•-</sup> pair ( $k_{ET(\text{CR})} = 2.1 \times 10^6$  s<sup>-1</sup>).<sup>[25]</sup> It is worth noting that the  $k_{ET(\text{CS})}$  for alkynyl-linked ZnP-[60]fullerene conjugates were found to be larger compared to other spacers (such as amides) due to the larger electronic coupling in the dyad.

## Conclusions

A new strategy to access porphyrin building blocks for palladium cross-coupling reactions has been developed. A zinc porphyrin, bearing a triflatophenyl groups in *meso*-position (ZnP-OTf), has been proposed as a useful alternative to the corresponding halophenylporphyrin, because of the much easier purification of the former.

We further showed that ZnP-OTf can be readily converted into the corresponding alkynylphenylporphyrins through a microwave-assisted Sonogashira cross-coupling protocol in relatively short times and excellent yields. The ZnP-OTf was further exploited in the preparation of a [60]fullerene based, donor-acceptor dyad in which an alkynyl spacer was used as the molecular wire between the zinc porphyrin and a fulleropyrrolidine. The strategy developed in this work could lead to the use of other triflatophenylporphyrins (such as the A<sub>2</sub>B<sub>2</sub> isomers) in preparation of donor-acceptor triads.

Given the wide range of metal-catalyzed cross-coupling reactions that were previously used to integrate halophenylporphyrin into nanoscale and mesoscale structures, the triflatophenylporphyrins are promising building blocks that should facilitate the preparation of e.g. light-harvesting arrays, nanorotors and molecular quantum bits.

## Experimental Section

### Materials and Methods:

Chemicals were purchased from Merck Millipore or Avantor VWR and used as received. Solvents were purchased from Merck Millipore and Avantor VWR, and deuterated solvents from Merck Millipore and Cambridge Isotope Laboratories. Thin layer chromatography (TLC) was conducted on pre-coated aluminum sheets with 0.20 mm Machevery-Nagel Alugram SIL G/UV254 with fluorescent indicator UV<sub>254</sub>. Column chromatography was carried out using Merck silica gel 60 (particle size 40–63 μm).

<sup>1</sup>H and <sup>13</sup>C NMR spectra were measured using a Bruker 500 Avance III and Bruker 400 Avance III HD. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent peak. Coupling constants (*J*) are given in hertz (Hz). Melting points are uncorrected. Mass spectrometry was performed by Susanna Vogliardi at the Department of Pharmaceutical and Pharmacological Sciences (University of Padova) with a Xevo G2-S QToF (Waters)

coupled with a UPLC system Acquity H Class (Waters). Single-crystal X-ray measurements reported have been deposited at the CCDC database.

Deposition Numbers 2265874 (for ZnP-OTf) and 2265873 (for ZnP-TMSA) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Absorption spectra were measured on a Cary 60 UV/VIS spectrophotometer using 1 cm quartz cuvettes and were baseline corrected. Emission spectra were recorded at room temperature with a FLS1000 UV/VIS/NIR spectrometer by Edinburgh Instruments and were collected exciting at 429 nm with a Xe lamp and using a PMT-850 detector. The absolute photoluminescence quantum yields were measured on a Hamamatsu Quantaurus-QY integrating sphere. Microwave irradiation was performed using CEM Discovery Reactor, using a dynamic mode of 200 W maximum power.

Cyclic voltammeteries were recorded in a three-electrode cell with a BASi C3 cell stand potentiostat, employing nitrogen purged 0.5 mM solutions of the analytes (ZnP-C<sub>60</sub> or ZnP-TMSA) in benzonitrile with 0.1 M *n*-Bu<sub>4</sub>PF<sub>6</sub> supporting electrolyte. A 1.6 mm diameter gold was used as working electrode (polished with a diamond paste and rinsed with acetone before every scan), with a platinum counter electrode and a Ag/AgCl reference electrode; potentials were then converted vsFc<sup>+</sup>/Fc couple by registering a CV scan of a ferrocene solution in the same medium as an external reference; the scan rate employed was 0.1 Vs<sup>-1</sup>.

Density functional theory (DFT) calculations were performed using the Gaussian 16 software package.<sup>[26]</sup> DFT calculations were performed using the hybrid functional B3LYP,<sup>[27]</sup> the 6-31G\* basis set for C, H and N atoms, while LanL2DZ<sup>[28]</sup> for the Zn atom in benzonitrile (PCM solvation).<sup>[29]</sup>

## Synthetic procedures

**4-Formylphenyl trifluoromethanesulfonate:** To a solution of 4-hydroxybenzaldehyde (5.0 g, 40.9 mmol) in pyridine (10 mL) at 0 °C, triflic anhydride (7.58 mL, 45.0 mmol) was added dropwise at 0 °C and the mixture stirred for 10 minutes at that temperature. The mixture was then stirred at r.t. for 12 h, then diluted with CH<sub>2</sub>Cl<sub>2</sub> and washed with 0.2 M aq. HCl and 0.2 M aq. K<sub>2</sub>CO<sub>3</sub> solutions. The organic layer was washed with H<sub>2</sub>O, dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO<sub>2</sub>, 9:1 hexanes-EtOAc v/v) and the desired product obtained as a colorless liquid (8.8 g, 85 % yield).

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*): δ 10.05 (s, 1H), 8.00 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 8.7 Hz, 2H). <sup>19</sup>F NMR (376 MHz, Chloroform-*d*): δ -72.74. <sup>13</sup>C NMR (126 MHz, Chloroform-*d*): δ 190.05, 153.18, 135.89, 131.71, 118.66, 109.99. MS (ES): found 254.0 [M]<sup>+</sup>, C<sub>8</sub>H<sub>5</sub>F<sub>3</sub>O<sub>4</sub>S requires 253.99. These characterizations are in accordance with data reported in the literature.<sup>[30]</sup>

**Zinc(II) 5,10,15-Trimesityl-20-(4-triflatophenyl)porphyrin (ZnP-OTf):** A solution of 4-formylphenyl trifluoromethanesulfonate (0.68 g, 2.66 mmol), mesitaldehyde (1.18 mL, 7.98 mmol) and pyrrole (0.74 mL, 10.64 mmol) in CHCl<sub>3</sub> (1.0 L, containing 0.75 % EtOH) was purged with Ar for 15 minutes before BF<sub>3</sub>·OEt<sub>2</sub> (0.50 mL, 3.54 mmol) was added. After 1 h at r.t., *p*-chloranil (2.04 g, 8.13 mmol) was added and the reaction mixture was left stirring. After 1 h, Et<sub>3</sub>N (490 μL, 3.54 mmol) was added, and the solution was evaporated to dryness. The crude product was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and passed through a SiO<sub>2</sub> plug (CH<sub>2</sub>Cl<sub>2</sub>). The porphyrin mixture was dissolved in CHCl<sub>3</sub> (50 mL) and metalated with a methanolic

solution of Zn(OAc)<sub>2</sub>·H<sub>2</sub>O (438 mg, 2.00 mmol) under stirring overnight in the dark. The reaction mixture was washed with 0.1 M aq. NaHCO<sub>3</sub> solution, dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated under reduced pressure, affording the zinc porphyrins mixture as a purple solid. The porphyrins mixture was purified by column chromatography (SiO<sub>2</sub>, first hexane-CH<sub>2</sub>Cl<sub>2</sub> 85:15 v/v, followed by hexane-ethyl acetate 95:5 v/v→90:10 v/v) to obtain the porphyrins A<sub>4</sub> (187 mg, 8 % yield), A<sub>3</sub>B (213 mg, 8 % yield), A<sub>2</sub>B<sub>2</sub> (*trans*- and *cis*-, 85 mg, 3 % yield), and the AB<sub>3</sub> (23 mg, 1 % yield). Crystals suitable for X-ray determination of ZnP-OTf were obtained by slow evaporation of a CHCl<sub>3</sub>/methanol solution.

m.p. > 250 °C. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*): δ 8.79 (d, *J* = 4.6 Hz, 2H), 8.75 (d, *J* = 4.6 Hz, 2H), 8.72 (s, 4H), 8.31 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.29–7.27 (m, 6H), 2.64 (s, 8H), 1.85 (s, 6H), 1.84 (s, 12H). <sup>19</sup>F NMR (376 MHz, Chloroform-*d*): -72.61. <sup>13</sup>C NMR (100 MHz, Chloroform-*d*): δ 150.11, 150.04, 149.80, 149.39, 149.30, 143.53, 139.25, 139.24, 138.87, 138.82, 137.51, 137.49, 135.64, 131.49, 131.37, 131.26, 131.02, 127.68, 120.27, 119.37, 119.18, 119.11, 117.25, 21.76, 21.67, 21.47. MS (ES): found 951.2508 [M + H]<sup>+</sup> and 983.2420 [M + CH<sub>3</sub>OH + H]<sup>+</sup>, C<sub>54</sub>H<sub>45</sub>F<sub>3</sub>N<sub>4</sub>O<sub>3</sub>SZn requires 950.2456.

**Zinc(II) 5,10,15-Trimesityl-20-(4-iodophenyl)porphyrin (ZnP-I):** A solution of 4-iodobenzaldehyde (0.50 g, 2.72 mmol), pyrrole (0.76 mL, 10.88 mmol) and mesitaldehyde (1.21 mL, 8.16 mmol) in CHCl<sub>3</sub> (1.0 L, containing 0.75 % EtOH) was degassed by bubbling Ar for 30 minutes. BF<sub>3</sub>·Et<sub>2</sub>O (0.9 mL) was added and the solution was stirred for 1 h, under dark. DDQ (1.85 g, 8.16 mmol) was added and all was stirred for 1 h. Then, Et<sub>3</sub>N (0.7 mL) was added, the reaction mixture was concentrated to about 200 mL and passed through a silica plug (hexanes-CH<sub>2</sub>Cl<sub>2</sub> 1:1 v/v) to recover a mixture of porphyrins. The mixture was then dissolved in CHCl<sub>3</sub> (20 mL) and 5 mL of sat. MeOH solution of Zn(AcO)<sub>2</sub>·2H<sub>2</sub>O was added in the dark and all was stirred at r.t. for 2 h. The reaction mixture was diluted with CHCl<sub>3</sub> and the organic phase washed with H<sub>2</sub>O, brine, dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated under reduced pressure. The crude was purified by repetitive column chromatography (SiO<sub>2</sub>, CHX/CH<sub>2</sub>Cl<sub>2</sub> 85:15 v/v) to obtain the product as bright pink solid (201 mg, 7 % yield).

m.p > 250 °C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*): δ 8.84 (d, *J* = 4.6 Hz, 2H), 8.77 (d, *J* = 4.5 Hz, 2H), 8.70 (s, 4H), 8.07 (d, *J* = 7.8 Hz, 2H), 7.96 (d, *J* = 7.8 Hz, 2H), 7.31–7.25 (m, 6H), 2.64 (s, 9H), 1.86 (s, 6H), 1.84 (s, 12H). MS (HRMS +): found 929.2056 [M]<sup>+</sup>, C<sub>53</sub>H<sub>45</sub>IN<sub>4</sub>Zn requires 929.2053. Characterization in accordance with literature.<sup>[31]</sup>

**Zinc(II) 5,10,15-Trimesityl-20-[4-[2-(trimethylsilyl)ethynyl]phenyl]porphyrin (ZnP-TMSA):** To a microwave vessel, a solution of zinc(II) 5,10,15-trimesityl-20-(4-triflatophenyl)porphyrin (50.0 mg, 53.7 μmol) in DMF/Et<sub>3</sub>N (5:1 v/v, 6.0 mL) was added and the solution was purged with a stream of argon for 10 minutes. During purging, [Pd(PPh<sub>3</sub>)<sub>4</sub>] (9.2 mg, 8.0 μmol), PPh<sub>3</sub> (4.1 mg, 15.6 μmol), and TMSA (14.9 μL, 107.4 μmol) were added to the vessel. The microwave vessel was sealed and immediately placed in the microwave reactor for heating at 120 °C for 60 minutes. The reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> and washed with 5 % LiCl (aq., to aid with the removal of DMF) and water, the organic phase dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated under reduced pressure. The mixture was purified by column chromatography (SiO<sub>2</sub>, hexanes/dichloromethane, 85:15 v/v) to afford a dark purple solid (45.0 mg, 93 % yield). Crystals suitable for X-ray were obtained by slow evaporation of a CHCl<sub>3</sub>/pyridine solution.

m.p. > 250 °C. <sup>1</sup>H NMR (500 MHz, Dichloromethane-*d*<sub>2</sub>): δ 8.86 (d, *J* = 4.6 Hz, 2H), 8.76 (d, *J* = 4.6 Hz, 2H), 8.72 (s, 4 H), 8.20 (d, *J* = 7.6 Hz, 2H), 7.86 (d, *J* = 7.6 Hz, 2H), 7.31 (s, 6 H), 2.64 (s, 9 H), 1.84 (s, 6H), 1.82 (s, 12H), 0.39 (s, 9 H). MS (HRMS) found 899.3469 [M + H]<sup>+</sup>,

C<sub>58</sub>H<sub>54</sub>N<sub>4</sub>SiZn requires 898.3409. These characterizations are in accordance with data reported in the literature.<sup>[16]</sup>

**Zinc(II) 5,10,15-Trimesityl-20-[4-[2-(4-formylphenyl)ethynyl]phenyl]porphyrin (ZnP-Ph-CHO):** A solution of ZnP-OTf (50.0 mg, 53.7 μmol) in DMF/Et<sub>3</sub>N (5:1 v/v, 6.0 mL) was introduced into a microwave vessel, and the solution purged with a stream of argon for 10 min. During purging, [Pd(PPh<sub>3</sub>)<sub>4</sub>] (9.2 mg, 8.0 μmol), PPh<sub>3</sub> (4.1 mg, 15.6 μmol), and 4-ethynylbenzaldehyde (10.4 mg, 80.5 μmol) were added. The vessel was sealed, placed in the microwave reactor and heated at 120 °C for 60 min. The reaction mixture was then diluted with CH<sub>2</sub>Cl<sub>2</sub> and washed with 5% LiCl (aq) and water; the organic phase dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated under reduced pressure. The crude was purified by column chromatography (SiO<sub>2</sub>, hexanes-ethyl acetate, 85:15 v/v) to afford a dark purple solid (44.1 mg, 88% yield).

m.p. > 250 °C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*): δ 10.10 (s, 1H), 8.88 (d, *J* = 4.6 Hz, 2H), 8.80 (d, *J* = 4.6 Hz, 2H), 8.73 (s, 4H), 8.27 (d, *J* = 8.1 Hz, 2H), 7.97 (apparent t, *J* = 8.3 Hz, 4H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.31–7.29 (m, 6H), 2.65 (s, 9H), 1.87 (s, 6H), 1.86 (s, 12H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*): δ 191.64, 150.14, 150.11, 149.90, 149.64, 144.07, 139.42, 139.12, 139.04, 137.60, 135.67, 134.68, 132.40, 131.89, 131.40, 131.32, 130.97, 130.12, 129.87, 127.80, 121.69, 119.16, 119.03, 93.86, 89.60, 29.86, 21.91, 21.82, 21.62. MS (HRMS) found 930.3182 [M]<sup>+</sup>, C<sub>62</sub>H<sub>50</sub>N<sub>4</sub>OZn requires 930.3276.

**Zn porphyrin-C<sub>60</sub> dyad (ZnP-C<sub>60</sub>):** A solution of ZnP-Ph-CHO (40.0 mg, 42.9 μmol), *N*-methylglycine (15.3 mg, 171.6 μmol), and [60]fullerene (123.6 mg, 171.6 μmol) in toluene (120 mL) was heated at 120 °C for 16 h. The mixture was cooled to r.t. and concentrated under reduced pressure. The mixture was purified by column chromatography (SiO<sub>2</sub>, toluene to recover the excess of [60]fullerene and then toluene-ethyl acetate 9:1 v/v to isolate the product). The fractions containing the ZnP-C<sub>60</sub> dyad were evaporated under reduced pressure and the product, dissolved in the minimum amount of CH<sub>2</sub>Cl<sub>2</sub>, precipitated with CH<sub>3</sub>OH, to give pure ZnP-C<sub>60</sub> as a purple powder (38 mg, 53% yield).

m.p. > 250 °C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*): δ 8.87 (d, *J* = 4.6 Hz, 2H), 8.78 (d, *J* = 4.6 Hz, 2H), 8.73 (s, 4H), 8.22 (d, *J* = 8.1 Hz, 2H), 7.92 (m, 4H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.29 (m, 6H), 5.03 (d, *J* = 9.3 Hz, 1H), 5.01 (s, 1H), 4.32 (d, *J* = 9.3 Hz, 1H), 2.89 (s, 3H), 2.65 (s, 9H), 1.87 (s, 6H), 1.86 (s, 12H). MS (HRMS) found 1680.3689 [M]<sup>+</sup>, C<sub>124</sub>H<sub>57</sub>N<sub>5</sub>Zn requires 1680.3938.

## Supporting Information

The authors have cited additional references within the Supporting Information (Ref. [32]).

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## Conflict of Interests

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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