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Molecular porphyrinic freestanding buckypaper electrodes from carbon nanotubes for glucose fuel cells

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An original strategy for the design of free standing buckypaper using unique molecular catalysts was developed. Pyrene-modified metalloporphyrin enable the formation of stable buckypaper using carbon nanotubes for the oxidation of glucose and reduction of oxygen. The developed molecular buckypapers show high performances and an excellent stability in a glucose fuel cell setup.

Introduction

Harvesting energy from natural sources has received much attention due to the rapidly globe's growing energy needs and problems. Efforts to develop new eco-friendly sources are therefore highly desirable. In this regard, glucose has been considered as a promising alternative to green energy for the direct conversion of its chemical energy to electrical energy.¹ In this context, two approaches have been extensively investigated. One is based on noble metals and metal alloys as active glucose catalysts, such as platinum and gold. Noble metals have been used as the most common catalysts for glucose fuel cells (GFCs), despite their high costs and quantities needed, in their use in GFC devices in order to achieve reasonable power energy.² Unfortunately, these metallic catalysts still suffer from sluggish kinetics, high cost, and low stability, especially, due to the well-known poisoning problems³⁻⁵ which presently limit their commercial applications.⁴⁻⁷ Another way toward the same ultimate goal is to convert glucose using enzymatic catalysts. Thanks to their natural specificity and selectivity, enzyme was extensively explored, but problems plaguing such biocatalysts still exist including the generated low power and the finite lifespan

originated from the proteinaceous fragility character which makes them unsuitable for long-term applications.⁸⁻¹¹ The complicated electrical connection of enzyme redox active center onto electron collectors represents an additional big obstacle for their integration in GFC. Therefore, replacement of the aforementioned catalysts with innovative catalysts, which are of low cost, high catalytic activity, stable, and robust, has become one of the key challenges for the development of GFC.

A new alternative is the use of molecular catalyst as an energy harvester, which allows to combine the metallic catalyst efficiency with enzymatic catalyst selectivity to provide a better trade-off between performance and stability. Accordingly, extensive efforts have been made in recent years in increasing molecular catalysts performance by developing innovative solutions: the use of new support materials, and the optimization of electrode structure as well as fabrication methods.

An ideal molecular catalyst support should provide a high-surface area, insure a high porosity in order to allow mass transport to and from the catalysts, and provide a high electronic conductivity within the molecular catalyst layer. Carbon nanotubes (CNTs) are well known for their excellent combination of electrochemical properties and specific surface area for the efficient wiring of a large amount of catalyst which make them an ideal candidate electrode material in a FC design.^{12,13} Several papers have been attempted to optimize the synergetic effect between molecular catalyst design and CNT support in order to increase the performance in GFC configuration. For example, adsorption of porphyrins catalysts on multi-walled carbon nanotube (MWCNT)-based electrodes using a drop casting method¹⁴ or their non-covalent immobilization on MWCNT¹⁵ was attempted. In fact, even though the use of CNTs as a support can provide increased output performance, the optimization of their resulting architecture can drastically increase the energy conversion yields, leading to clearly improved current densities and stability. Confining molecular catalysts in a highly macroscopic 3D conducting, mesoporous matrix could considerably

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maximize the electron transfer and optimize the mass transport in the substrates.

In this context, CNTs can be shaped and assembled in macroscopic scale, such as fibers¹⁶, pellets¹⁷, or buckypapers (BPs)¹⁸, which make them easy to process into mesoporous electrodes in fuel cell designs. BPs are thin films of randomly entangled CNTs, leading to highly porous networks formed by the self-assembly, mainly due to van-der-Waals forces in the tube-tube junctions. There are several methods to fabricate the CNT-BP electrodes.^{19–21} The most widely used method is the vacuum filtration of the CNT dispersions, where the CNT quality and their homogeneous dispersion are crucial parameters to obtain stable free standing BP films.

Herein, we use pyrene-modified metalloporphyrin simultaneously acting as molecular electrocatalysts and macromolecular cross-linking units for MWCNTs in order to produce scalable free standing molecular redox-BP electrodes. The multiple non-covalent binding between porphyrin pyrene units and MWCNTs is ensured through π -stacking interactions of the pyrene groups onto MWCNTs sidewalls. These interactions are expected to improve the formation of robust freestanding MWCNTs electrodes particularly suited for the electrocatalytic reaction without using any binder. Such BPs are capable of producing high power densities, because power scales with the catalyst loading and their high porosity as well as surface area allow large loadings of catalyst compared to flexible 2D film-based electrodes. The BP was made by mixing ~~from~~ commercial MWCNT homogenous dispersion and pyrene-modified porphyrin in organic media, followed by filtration of the resulting dispersion through a PTFE membrane. The efficiency of the fabricated BP was greatly improved through the synergy of the superior properties of MWCNTs and tailored macroscopic structure properties of the resultant BP.

Results and discussions

To design an enhanced configuration of a GFC, we describe the synthesis as well as the characterization of pyrene-functionalized cobalt tetracarboxyphenyl porphyrin (Co(TCPP)pyr₄) and rhodium tetracarboxyphenyl porphyrin (Rh(TCPP)pyr₄) complexes enabling the formation of the buckypaper for the reduction of oxygen and oxidation of glucose, respectively. Therefore, we opted to use a simple and general synthetic method in which pyrene groups were first covalently bonded to porphyrins via formation of amide functions using pyrene amine derivative as depicted in Fig. 1. The resulting product was then metallated to give the desired complexes. Thanks to the presence of four carboxylic groups, tetracarboxyphenyl porphyrin (TCPP) was used as the precursor reagent for the synthesis of pyrene-functionalized tetracarboxyphenyl porphyrin ((TCPP)pyr₄), in order to introduce multiple pyrene units in the final structure. In the resulting complex, the pyrene amine units bind to the porphyrin at four positions of the phenyl rings. Taking into account the close proximity of the porphyrin aromatic ring, an improved π - π stacking interaction with the sidewalls of CNTs

is expected to be much stronger and favourable to reinforce the BP mechanical stability. Experimentally, TCPP was first reacted with thionyl chloride to activate its carboxylic acids, then was allowed to react with the amine group of 1-pyrenemethylamine to form (TCPP)pyr₄.¹⁵ The latter was metallated using cobalt and rhodium salts to afford Co(TCPP)pyr₄ and Rh(TCPP)pyr₄ complexes, respectively (Fig. 1).

Fig. 1 Synthesis of pyrene-appended Co(TCPP)pyr₄ and (Rh(TCPP)pyr₄) for the BP fabrication.

Both Co(TCPP)pyr₄ and Rh(TCPP)pyr₄ were synthesized with the aim to produce BP electrodes via π -stacking interactions. These BPs were prepared via a simple filtration of MWCNTs dispersion in presence of Co(TCPP)pyr₄ or Rh(TCPP)pyr₄. Experimentally, commercial MWCNTs (15 mg) were dispersed in 100 ml of N-Methyl-2-pyrrolidone (NMP) and subjected to sonication for 20 min in order to form homogeneous suspension. Then, 5 mg of Co(TCPP)pyr₄ or Rh(TCPP)pyr₄ was added to the MWCNTs dispersion under magnetic stirring. After 1 hour, the mixture was then filtered under vacuum over a PTFE membrane filter with a pore size of $0.45\mu\text{m} \pm 0.1$. The formed MWCNTs film electrodes were rinsed with NMP, DMF and deionized water to remove any loosely bound and unbound components. The formed BP on a PTFE membrane was then dried in a vacuum oven at 80°C for 20 min and carefully peeled off from the surface of the filter. For instance, BP of a thickness of about 50 μm can be obtained after the filtration of 100 mL of the MWCNT/catalyst dispersion. It should be noted that BPs obtained from commercial MWCNT under identical conditions are very fragile and difficult to handle without the presence of pyrene-functionalized porphyrin as a cross-linker.

To investigate the BPs' proprieties, electron microscopy SEM and TEM were employed to observe their morphological changes. Fig. 2A presents a photograph of the as-obtained free standing BP with a good mechanic stability. Fig. 2B shows a representative SEM image of the as-prepared BPs. In this image, the MWCNTs are randomly oriented throughout the sample. Such an interesting structure has a high Brunauer–Emmett–Teller (BET) volume of $3\text{ cm}^3\text{ g}^{-1}$. Moreover, the electric resistance of the buckypaper was measured using a four-point probe and revealed a high conductivity of $25 \pm 3\text{ S}\cdot\text{cm}^{-1}$.

We have studied the filtration and adsorption of Co(TCPP)pyr₄ and Rh(TCPP)pyr₄ complexes quantitatively using UV-Vis. The

catalyst concentrations of original solutions (2.8 mM for Co(TCPP)pyr₄ and 2.9 mM Rh(TCPP)pyr₄) and outflow collections during the filtration period were monitored by UV-Visible spectra, in which Co(TCPP)pyr₄ and Rh(TCPP)pyr₄ complexes show characteristic Soret absorption band at a wavelength of 435 nm and 450 nm, respectively. After the filtration process, the absorption Soret peaks at 435 nm and 450 nm decrease significantly in the spectrum, indicating that adsorption of catalyst occurs. We estimated the adsorption quantity during the filtration process by calculating the absorption intensity ratio of the outflow liquid relative to original dispersion of MWCNT and Co(TCPP)pyr₄ or Rh(TCPP)pyr₄ dispersions (Figure S1). Experimentally, the MWCNT buckypaper retain 4.46 mg of Rh(TCPP)pyr₄ complex and 4.36 mg of Co(TCPP)pyr₄.

For transmission electron microscopy (TEM) observation, drops of dilute MWCNT suspension in THF with and without the Rh(TCPP)pyr₄ or Co(TCPP)pyr₄ complexes was deposited onto electron microscopy grids and allowed to dry. The graph in Fig. 2C represents the TEM image of the MWCNT sample without the porphyrin catalysts. In the graph in Fig. 2D and 2E a dark shadow around the MWCNTs sidewalls was observed and confirm the presence of a heavy dark coating compared to Fig. 2C without the porphyrins catalysts. It appears to be homogeneously distributed within the MWCNT network and located on the surface of the MWCNTs sidewalls. This might be due to porphyrins' multiple pyrene groups attached to the outer MWCNT wall enabling stable π - π -interactions. Their diameter was estimated to be between 1-2 nm. These observations could confirm the contribution of the π - π -interactions on the formation and stabilization of the BP structures.

Fig. 2 A) Photograph of the formed BP on a membrane filter. B) SEM image of the BP surface. C) TEM image of the MWCNT (D) TEM image of the Rh(TCPP)pyr₄-MWCNT (E) TEM image of the Co(TCPP)pyr₄-MWCNT.

The as-prepared BPs were finally cut into rectangular strips of a width of 1 cm and a small part of the BP was kept for the electrical contact. For all electrochemical investigations, these BP strips were connected with a clip and placed in a

conventional three-electrode electrochemical cell giving an effective geometric area (1 cm²) of the electrode in the electrolyte. Cyclic voltammetry (CV) was performed in a conventional three-electrode cell equipped with the BP as a working electrode with a geometric surface of 1 cm². A platinum wire was used as a counter-electrode and a saturated calomel electrode (SCE) as a reference. All potentials in this work were referred to the SCE. The solutions were deoxygenated by purging with argon prior to each experiment and an argon flow was kept over the solution during the whole experiment. The solutions were oxygenated by purging with oxygen gas prior to each experiment and an oxygen flow was kept over the solution during the whole oxygen reduction experiments. Rh(TCPP)pyr₄-BP was characterized using cyclic voltammograms (CVs) at room temperature. Fig. 3A shows the CVs in a 0.1 M KOH solution in absence of glucose recorded with Rh(TCPP)pyr₄-BP electrodes. Under these experimental conditions, the CV of the Rh(TCPP)pyr₄-BP displays a well-defined reversible redox system at $E_{1/2} = -0.33$ V, assigned to the Rh^{III}/Rh^I redox couple which is in good agreement with previous studies for Rh porphyrins-type catalysts.¹⁴ The intensities of both anodic and cathodic peaks are directly proportional to the scan rate as well as the peak separation is virtually zero, thus confirming the immobilization of the Rh(TCPP)pyr₄ with excellent electron transfer rates between adsorbed Rh(TCPP)pyr₄ and MWCNTs (inset, Fig. 3A). Integration of the oxidation or reduction of the Rh^{III}/Rh^I wave in the CV scans allows us to determine a maximum surface coverage of $\Gamma = 1.25 \pm 0.2$ $\mu\text{mol cm}^{-2}$ which is higher compared to previously reported BP-based molecular crosslinks using pyrene-cobaloximes derivatives immobilized on CNTs²² and pyrene-modified 2,2-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid)²³, thus highlighting the ability of straightforward multiple supramolecular functionalization of MWCNT to design a stable and high loading molecular electrodes. Such electrochemical behaviours turned out to be reproducible by using distinct BP electrodes and do not evolve with time.

We then investigated the Rh(TCPP)pyr₄-BP electrodes in the presence of glucose at room temperature. Initially, all electrodes were pretreated by repeated cycling at the potential range from -0.75 to 0.1 V at a sweep rate of 50 mV s⁻¹ before testing the glucose oxidation activity in order to remove any surface contaminants. Fig. 3B shows the CVs of a 0.1 M KOH solution containing different concentrations of glucose. Upon addition of increasing amounts of glucose, the increase of the intensity of the peak at $E_{1/2} = -0.33$ V corresponding to the oxidation of Rh^I to Rh^{III} confirms the occurrence of electrocatalytic oxidation of glucose by the immobilized Rh^{III}(TCPP)pyr₄. In addition, the current increased with an increase in the glucose concentration and reached a maximum current density of 5 ± 0.5 mA cm⁻² in the presence of 50 mM of glucose. Even though only 50 mM of glucose was used as mentioned above, the high current density was obtained which demonstrated an obvious enhancement in the current density and is in contrast to previously reported Rh porphyrins-CNTs under the same experimental conditions.¹⁴

The increased activity could be related directly to the amount of catalyst immobilized onto the MWCNT BPs. In addition, the onset of the polarization curve was determined to be -0.45 ± 0.2 V. This onset potential is considerably more negative than other previously reported molecular electrocatalysts, such as cobalt complexes²⁴⁻²⁶, ruthenium bipyridine complexes²⁷⁻²⁸, and nickel porphyrins²⁹⁻³⁰ and even comparable to those with metallic gold-based catalysts³¹ and gold porphyrin complexes³², although it is higher than those with Pt-based catalysts³³ and rhodium deuteroporphyrin.¹⁴ It should be noted that the catalytic anodic wave exhibits a twisted shape, i.e., a notable catalytic current decrease at higher potentials followed by current recovery upon reversing of the scan. This behaviour is caused by an electrocatalytic deactivation of Rh(TCPP)pyr₄ catalyst that occurs at increased potentials. On the reverse scan, the catalytic current is recovered by reductive regeneration/activation of the catalyst.¹⁴

Fig. 3 A) Cyclic voltammograms of as formed Rh(TCPP)pyr₄-BP at different scan rates: (a) 20, (b) 10, (c) 5, (d) 2 and (e) 1 mV s⁻¹. The measurements were performed in 1 M KOH solution (pH 14) and under argon. (Inset) Plot of peak currents vs scan rate. B) Cyclic voltammograms of Rh(TCPP)pyr₄-BP at a scan rate of 10 mV s⁻¹ in the presence of (black dotted) 0 mM, (green) 10 mM, (blue) 20 mM and (red) 50 mM glucose (Measurements were performed in 1 M KOH solution under a nitrogen atmosphere at 25 °C).

The electrocatalytic proprieties of Co(TCPP)pyr₄-BP towards oxygen reduction were also investigated at room temperature under an alkaline condition (0.1 M KOH). Fig. 4A shows the CVs of the Co(TCPP)pyr₄-BP at a scan rate of 5 mV s⁻¹ under argon, and oxygen. As expected, in the absence of oxygen (solution purged with argon), no cathodic catalytic current was obtained. The CV only exhibits the featureless high capacitive current of the Co(TCPP)pyr₄-BP. In contrast, a well-defined O₂ reduction peak centred at -0.12 V emerges in the electrolyte solution saturated with O₂ with an onset potential of -0.05 V for oxygen reduction. The latter is slightly positively shifted by approximately 60 mV compared with that observed with reported Pt/C catalyst under the same conditions.³⁴ In addition, Co(TCPP)pyr₄-BP exhibits a markedly high cathodic current value of -3.2 ± 0.3 mA cm⁻².

To gain further insight into oxygen reduction stability of our cathode, chronoamperometric measurements of Co(TCPP)pyr₄-BP were carried out to determine the catalytic current under full load discharge for about 3 hours (10500 s) at -0.15 V under argon and then oxygen saturated solution (Fig. 4B). Purging the solution with oxygen triggers an increase in

intensity of the cathodic current that rapidly stabilizes at -1.92 ± 0.2 mA cm⁻². After 3 h, the Co(TCPP)pyr₄-BP yielded a stable current density of -1.83 ± 0.2 mA cm⁻². It should be noted that the catalytic current decreased only by 5% after 3 h, illustrating the remarkable operational stability of this cathode. No visible degradation of the BP was observed over 3 h. This is likely due to the mechanical stability of the Co(TCPP)pyr₄-BP, which unambiguously evidenced the major role of the BP robust structure. Such an excellent durability of the cathode delivers a high performance that guarantees a long-term use with negligible current intensity loss.

Fig. 4 A) Cyclic voltammograms of the catalytic Co(TCPP)pyr₄-BP electrode at 5 mV s⁻¹ scan rate in (a) argon, and (b) O₂ saturated solution. The measurements were performed in 1 M KOH solution at room temperature. B) Chronoamperometric response for Co(TCPP)pyr₄-BP electrode before and after bubbling oxygen into the electrolyte. Experimental conditions: 0.1 M KOH solution at room temperature; applied potential -0.15 V.

Building on the promising features of the aforementioned cathodic and anodic performance demonstrated in a three-electrode cell under alkaline conditions, we construct and characterize its operation and durability in one-compartment membraneless alkaline glucose/O₂ fuel cells. Experimentally, the fuel cell characterization was evaluated by dipping the anodic and cathodic BPs in the presence of glucose (0.1 M KOH 0.5 mol L⁻¹) and under the supply of a constant oxygen gas flow within the solution. Fig. 5 displays the resulting polarization and power curves recorded during successive potentiostatic discharges of 30 min under stirring to remove the contribution of the capacitive current. The GFC shows an OCV of 0.45 ± 0.2 V which is in good agreement with the sum of OCV (0.42V) of the independently obtained values for each OCP determined for the anode (OCP_{anode} = -0.47 V) and the cathode (OCP_{cathode} = -0.05 V). By starting recording the polarization graph at the OCV (0.45V), the voltage decreases until reaching a maximum current density of 37 ± 5 mA cm⁻². The decrease of the voltage over the entire current range is mainly due to the inactivation behaviour of the Rh(TCPP)pyr₄ catalysts at high potentials as previously reported.²² The power curve, derived from the polarisation curve, gives access to the maximum power output density of 2.6 ± 0.3 mW cm⁻² at 0.22V. Remarkably, the overall fuel cell performances are the higher order of magnitude than all existing enzymatic glucose/O₂ fuel cells using different

electrode architectures. In addition, the present GFC performance is also higher than other fuel cell setups using either a cathodic or/and anodic noble metal or metal alloy. As a reference, the OCV and $P_{\max}$ have been reported to be 0.385 V and 0.196 mW cm^{-2} for an alkaline FC with an Ag anode³⁵, 1.3 V and 2.55 mW cm^{-2} for an alkaline FC with a NiO buckypaper³⁶ cathode and 0.65 V and 0.22 mW cm^{-2} for an alkaline FC with a silver-modified Au³⁷. Additionally, without considering different experimental conditions, these reported metallic electrodes have a loading superior in terms of metal catalytic sites compared to our electrode. However, absolute fuel cell performance might be enhanced by increasing the Co(TCPP)pyr₄ and Rh(TCPP)pyr₄ loading, which is less expensive compared to metal or metal alloys catalysts.

It should be noted that the buckypaper-molecular fuel cell required only 0.075 mg cm^{-2} of cobalt metal and 0.120 mg cm^{-2} of Rh metal. These loadings of metal are approximately 50 times below the amount of catalytic metal used for the aforementioned noble metal electrodes highlighting the great utility of the concept of buckypaper-based molecular catalyst for glucose/O₂ fuel cell, especially when using noble.

Indeed, on a metal point of view, the cathodic Co(TCPP)pyr₄ and anodic Rh(TCPP)pyr₄ catalysts considerably outperform the aforementioned reported GFCs as a function of mass activity (mW/g).

Fig. 5 Polarization curve and power density curve at room temperature for a glucose–O₂ fuel cell. Anode: Rh(TCPP)pyr₄-BP. Cathode: Co(TCPP)pyr₄-BP. 0.5 M of glucose, 0.1 M KOH.

We finally investigate the long-term stability of the GFC by periodically recording the power density during 30 days. The fuel cell still delivered a maximum power density of 1.5 mW cm^{-2} after 30 days, which represents approximately 58% of its initial activity and constitutes one of the highest stability reported for an alkaline GFC.

To the best of our knowledge, this is the first report on the fuel cell using the BPs fabricated from uniquely molecular catalysts at both, the cathode and the anode, without any binder. The BP configuration shows the highest catalytic activity, suggesting both electrode design and catalyst immobilization synergistically contribute to enhance the catalytic activity. On

one hand, the BP architecture based on the non-covalent interactions has a considerably large specific surface volume, an increased porosity and a high conductivity: these desirable features promote the electron transfer and facilitate mass transport and diffusion (fuel and electrolyte) in the system. On the other hand, the molecular cathodic and anodic catalysts strongly immobilized via multiple π – π stacking enhance the formation of a robust 3D structure, which provides a stable structure for the long-term operation of the fuel-cell.

Conclusions

In conclusion, a simple, scalable and especially facile strategy has been developed for fabricating non-enzymatic and precious-metal free GFC using BP based molecular catalysts. The BPs show individually enhanced electrocatalytic properties towards glucose oxidation reaction and oxygen reduction reaction with a high stability. The as-designed GFC using the anodic and cathodic molecular catalyst BP electrodes significantly outperformed the metallic and enzymatic GFC in the output power density. This innovative approach might boost further studies to explore BP-based molecular catalysts for a variety of applications.

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Notes and references

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Supporting information for:

Molecular porphyrinic freestanding buckypaper electrodes from carbon nanotubes for glucose fuel cells

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1. Materials and Instrumentation:

Chemicals used in this work were purchased from Sigma-Aldrich and used as received unless mentioned otherwise.

The morphology was observed using scanning electron microscopy SEM (JEOL, JSM-6700F, 5 kV) and TEM (JEOL, JEM-2010, 200 kV). Nuclear magnetic resonance (NMR) spectroscopy was carried out with Bruker Avance 400 NMR spectrometer operating at 400.0 MHz. ESI mass spectra were recorded with a Bruker APEX-Qe ESI FT-ICR mass spectrometer. Brunauer–Emmett–Teller (BET) specific surface area of samples was measured at 77 K with a Micromeritics ASAP 2020 HD88 system. The electric resistance was measured by a DC voltage/current four-point probe method using a Jandel (RM3). UV-vis spectra were measured using a

UV-1500 PC photodiode array spectrophotometer equipped with a quartz cell (light path = 1 cm).

All Electrochemical measurements were performed at room temperature with an Autolab electrochemical analyzer (Eco Chemie, Utrecht, and The Netherlands).

Synthesis:

the synthesis and characterization of Co(TCPP)pyr₄ have been previously described.^[15] The synthesis of Rh(TCPP)pyr₄ was performed by slightly modifications of established literature reported method^[15] using the following procedure: Meso-tetrakis-(4-carboxyphenyl) porphyrin (100 mg, 0.125 mmol) was dissolved in 10 ml of anhydrous methylene chloride. 1.5 ml of a 2 M solution of oxalyl chloride in methylene chloride (3 mmol) and a catalytic amount of DMF (1 μ l) was added. The mixture was stirred overnight under nitrogen. After concentrating the solution in a stream of dry nitrogen then under high vacuum, the crude acid chloride was redissolved in 10 ml of dry DMF. A solution of the pyrenemethylamine (227.7 mg, 1 mmol, 8 equivalents) and 500 μ l of triethylamine in 5ml of dry DMF were added. The resulting mixture was stirred under nitrogen overnight. The solution was concentrated and respectively washed with 10% citric acid, 1N NaOH, and dichloromethane (50 mL). The crude product was dissolved again in 50 ml of dry DMF and Rh₂Cl₂(CO)₄ (15.0 mg) was added, stirred and refluxed for 7 h. After evaporation of the solvent, column chromatography was eluted with dichloromethane then dichloromethane/ethanol (15:1) to afford the desired Rh(TCPP)pyr₄ complex (29 mg).

¹H NMR (400 MHz, DMSO-d₆, δ): 9.78 (s, 4H), 8.91 (s, 8H), 8.59-7.86 (m, 44H), 7.66 (d, 4H), 7.58 (d, 4H), 5.44 (d, 8H).

MS (ESI) (DMSO) m/z: [Rh(TCPP)pyr₄]⁺ calcd for C₁₁₆H₈₀N₈O₄Rh, 1752.5; found, 1752.9.

Figure S1. UV spectra of A: Rh(TCPP)pyr₄ a) solution before filtration b) outflow collection solution (Inset before and after adding MWCNT to an initial solution of Rh(TCPP)pyr₄) . B) Co(TCPP)pyr₄ a) solution before filtration b) outflow collection solution. The measurements were performed in DMF.