

Catalytic Activity Towards Hydrogen Evolution Dependent of the Degree of Conjugation and Absorption of Six Organic Chromophores

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Conjugated materials can, in many cases, absorb visible light because of their delocalized π electron system. Such materials have been widely used as a photoactive layers in organic photovoltaic devices and as photosensitizers in dye-sensitized solar cells. Additionally, these materials have been reported for applications in solar fuel production, working as photocatalysts for the hydrogen evolution reaction (HER). The synthesis of three flexible vinyl groups-containing chromophores is reported. The catalytic activity towards hydrogen evolution of these chromophores has been investigated and compared to their non-vinyl-containing analogues. The catalytic effect was confirmed using two different approaches: electrochemical, using the chromophores to modify a working electrode, and photocatalytic, using the chromophores combined with platinum nanoparticles. A relationship between the degree of conjugation and the catalytic activity of the chromophores has been observed with the electrochemical method, while a relationship between the UV absorption in the solid state and the photocatalytic effect with platinum nanoparticles was observed.

Hydrogen is coming up to the stage of widespread use, not only because of its large energy density and its easy production but also because it is the cleanest energy carrier and most environmentally friendly fuel.^[1] The hydrogen evolution reaction (HER) is of prime importance for fundamental and applied

electrocatalysis. By far, platinum-based catalysts have been considered as the most essential catalysts for HER.^[2] However, their high cost and scarcity hamper a widespread use for hydrogen production and in hydrogen fuel cells,^[3] leaving a demand for low-cost alternative catalysts for hydrogen evolution. Although most studies are focused on inorganic semiconductors as catalysts for hydrogen evolution, very promising approaches from communities around the world based on metal-free organic catalysts for the hydrogen evolution reaction have been reported.^[4]

The vast interest in organic chromophores is driven by their potential for the manufacture of cheap and efficient electronic devices such as photovoltaic cells and light-emitting diodes.^[5] Organic chromophores may also act as electrocatalysts in various processes.^[6] The promising potential of organic highly conjugated chromophores having narrow π - π^* energy gaps is mostly directed towards solar-energy conversion into clean H₂ fuel by water splitting.^[7,8] The pioneering report on conjugated photocatalysts [linear poly(*p*-phenylene)s (PPPs)] for H₂ evolution can be traced back to a publication in 1985 from Yanagida and co-workers.^[9] In addition, suitable metal **co-catalysts**, mostly platinum nanoparticles, have been used to lower the redox overpotential and improve **charge transfer and separation**, which has greatly enhanced the photocatalytic performance of organic catalysts.^[10] However, literature data on using these chromophores for hydrogen evolution without platinum support is extremely limited.

Electrochemical hydrogen evolution from water is regarded as one of the most sustainable techniques for production of high-purity H₂. The HER is a fundamental step in electrochemical water splitting that requires a cost-effective and long-lasting catalyst to overcome the energy barrier of the reaction.^[11–13] Catalysts in powder form that can be used as materials to modify electrodes and are highly active and stable in acidic solutions are suitable as materials for electrochemical investigation of the HER. Enormous efforts have been dedicated to the development of such catalysts; however, there are hardly any reports, except for Pt-based catalysts.^[14]

Herein, we describe three different types of highly conjugated organic molecules (two tri- and four tetracarboxylic acids) based on three different cores (triphenylamine, anthracene and tetraphenylethylene) that can be used with or without platinum nanoparticles as catalysts in hydrogen evolution reactions. Benefiting from their carboxylic groups, these compounds can also serve as ligands in metal complexes

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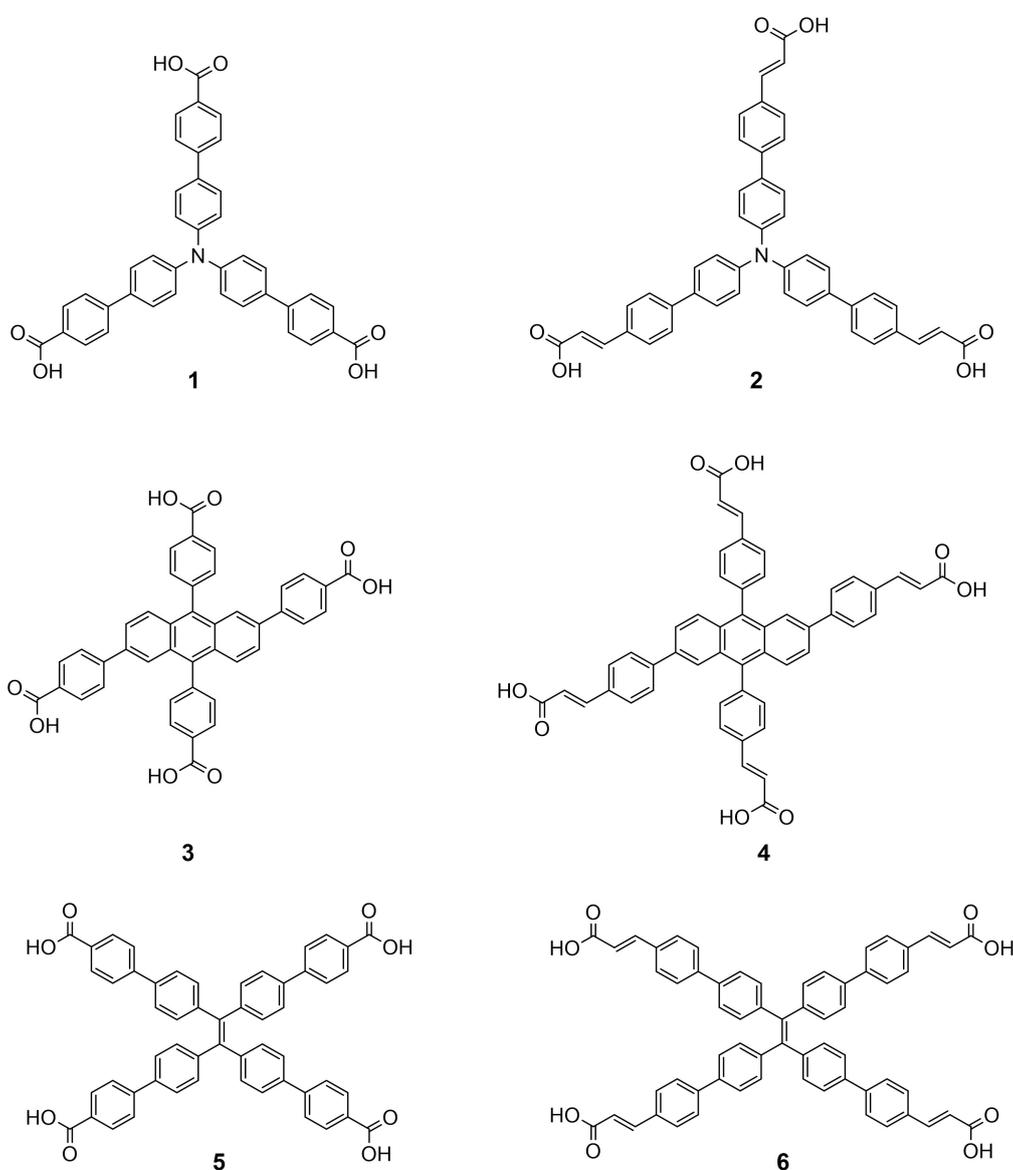
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or as linkers in metal-organic frameworks (MOFs) or coordination polymers.

 Dear Author, Scheme 1 is not mentioned in the text.

The flexibility and degree of conjugation of compounds **2**, **4**, and **6** were modified by including a vinyl group between the carboxylic acid and the aromatic moiety. This was achieved by using [4-(*E*-3-methoxy-3-oxo-1-propen-1-yl)phenyl]boronic acid, prepared according to the literature via Knoevenagel condensation,^[15] in the corresponding Suzuki-Miyaura cross-coupling reactions (available in ESI). Extending the degree of conjugation with a vinyl group was chosen mostly due to practical reasons. Ligands constructed from repeating phenyl rings sometimes lead to anticipated practical problems, like low yields, solubility problems etc.

In order to elucidate the electrocatalytic activity in HER of the above-mentioned chromophores, linear sweep voltammetry was used to study the unmodified glassy carbon (GC) electrode and this electrode modified with the corresponding chromophores **1**–**6**. The data in Figure 1 show that the modification of the GC electrode leads to increased activity of HER relative to the bare electrode. Interestingly, increase of the HER activity dependent on the number of phenyl rings and degree of conjugation was observed. The triphenylamine derivatives (compounds **1** and **2**) composed of six phenyl rings showed the lowest catalytic activity, followed by the anthracene derivatives composed of seven phenyl rings. In particular compound **6**, which proved to be the best catalyst among these chromophores, composed of eight phenyl rings, displays a drop in the onset potential for HER of more than 200 mV in comparison with GCE.



Scheme 1. The six different chromophores based on triphenylamine (**1** and **2**), anthracene (**3** and **4**), and tetraphenylethylene (**5** and **6**).

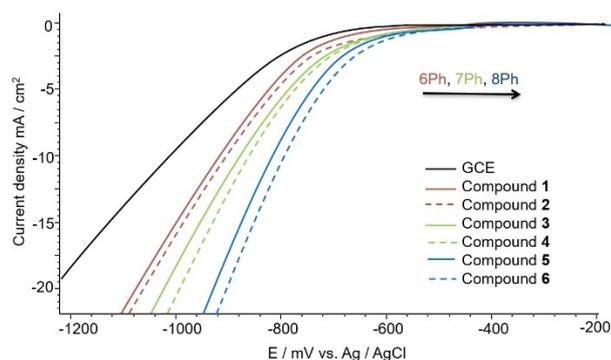


Figure 1. Polarization curves for hydrogen evolution in 0.5 M H₂SO₄ on various electrodes.

Furthermore, as can be seen in Figure 1, every derivative that contains vinyl groups shows a slightly higher catalytic activity towards HER compared to the non-vinyl-containing analogue. These electrochemical studies indicate that the hydrogen evolution is dependent on the degree of conjugation in compounds 1–6.

The electrochemical stability of the electrode modified with compounds 1–6 was confirmed by consecutive measurements. After ten polarization sweeps the electrode retained a polarization curve similar to the initial one. Experiments were also repeated after the samples (catalysts on an electrode immersed in 0.5 M sulfuric acid aqueous solution) were kept in the refrigerator for two weeks and only negligible loss of cathodic current density was observed. Additionally, after the consecutive measurements, elemental analysis of the compounds was repeated and confirmed that the compounds stayed intact.

In order to confirm the catalytic effect of 1–6, additional experiments were conducted using the chromophores together with platinum nanoparticles to study their photocatalytic activity towards HER in an aqueous methanol solution.

Also, solid-state UV/Vis spectroscopy was applied in order to get a better understanding of the photocatalytic activity (Table 1). Although no correlation with the rate of hydrogen evolution is observed, the photocatalytic experiments show that the catalytic effect of the chromophores together with platinum nanoparticles is closely related to the absorption of 1–6 at 420 nm in the UV/Vis spectra (Figure 2). Compound 2 has the most pronounced effect on the catalytic activity. This can be attributed to strong interactions of the Pt nanoparticles with

Table 1. UV absorption (solid state) and hydrogen evolution rate of compounds 1–6.^[a]

Compound	UV absorption solid state/ nm	Hydrogen evolution rate/ $\mu\text{mol min}^{-1}$
Compound 1	400	42.6
Compound 2	410	32.8
Compound 3	390	27.6
Compound 4	405	13.4
Compound 5	410	9.5
Compound 6	420	23.8

^[a] For experimental details see Supporting Information.

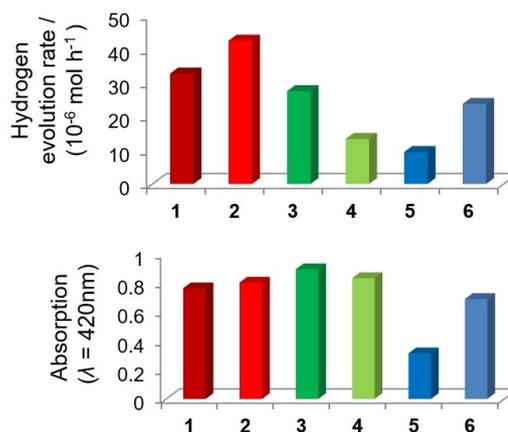


Figure 2. Correlation between the absorption at 420 nm and catalytic activity in HER.

N-containing groups.^[16,17] Although, to the best of our knowledge, there is no literature supporting the fact that Pt nanoparticles modified with N-containing conjugated molecules enhance the catalytic activity towards HER, it has been proven that the presence of N-containing functional groups can lead to a high dispersion of Pt nanoparticles with a synergistic interaction of Pt and support, resulting in improved catalytic activity and durability toward oxygen reduction reaction and methanol oxidation reaction.^[18]

This effect is most pronounced for the tetraphenylethylene compounds (compounds 5 and 6), where the vinyl-containing chromophore showed a three-fold increased catalytic effect towards HER compared to the non-vinyl analogue. A similar effect can be observed for the absorption at 420 nm. In the case of the anthracene-based functional dyes (compounds 3 and 4), the catalytic rate of the non-vinyl group-containing compound is higher than the vinyl group-containing one, and so is the absorption at 420 nm. The same effect is found for the triphenylamine-based functional dyes (compounds 1 and 2).

In conclusion, organic conjugated chromophores (1–6, Figure 1) can act as electrocatalysts for hydrogen evolution from water in acidic electrolytes and also in photocatalytic hydrogen generation from aqueous methanol solution in combination with platinum nanoparticles. When applied alone, these chromophores show a linear dependence in their catalytic activity from their degree of conjugation. It appears that interactions between these chromophores and platinum nanoparticles occur that are closely related to their activity. A correlation between the absorption at 420 nm and the catalytic activity of the chromophores in HER was observed. However, attempts to correlate the electronic structure with the catalytic activity were unsuccessful. Thus, while this is a very interesting observation, an explanation is still pending at this time. Nevertheless, these chromophores show potential to support hydrogen generation utilizing renewable energy sources such as wind or sunlight.

Supporting Information

The content of the SI includes the synthesis of compounds **2**, **4** and **6**, crystallographic data for compounds Me₃-**2** and Me₄-**6**, experimental details of the electrochemical and photocatalytic experiments, solid-state and solution (in dichloromethane) UV/Vis spectra of compounds 1–6.

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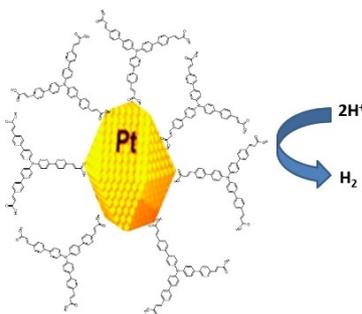
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The catalytic activity towards hydrogen evolution of three rigid and three flexible vinyl groups-containing chromophores was confirmed by electrochemistry (electrode modified with chromophores) and photocatalysis (chromophores combined with platinum nanoparticles). A relationship between the degree of conjugation and the UV/Vis absorption and the catalytic activity has been observed.



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Do the degree of conjugation and absorption of organic chromophores have an effect on the catalytic activity in hydrogen evolution reactions? Check out the work of our Board Chair @HayHawkins @UniLeipzig

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