Electronic supplementary information for:

Catalytic activity towards hydrogen evolution dependent on the degree of conjugation and absorption of six organic chromophores

1. General methods

^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature with a Bruker AVANCE DRX 400 spectrometer; chemical shifts are given in parts per million (ppm) at 400.13 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR). Internal standard was tetramethylsilane (TMS). Melting points were determined with a Gallenkamp MPD350.BM2.5 device. UV Vis spectra were obtained measured with a Perkin-Elmer Lambda 900 spectrometer. Elemental analyses were performed with a Vario El-Heraeus analyser. The crystallographic data for Me$_3$-**2** and Me$_4$-**6** were collected on a Gemini diffractometer (Rigaku Oxford Diffraction) using Mo-Kα radiation (λ = 71.073 pm) and ω-scan rotation. Data reduction was performed with CrysAlis Pro including the program SCALE3 ABSPACK for empirical absorption correction. The structures were solved by dual-space methods with SHELXT-2014,[1] and the refinement of all non-hydrogen atoms was performed with SHELXL-2018[2] with anisotropic thermal parameters. For Me$_3$-**2** and Me$_4$-**6** all solvent molecules are disordered. The electron density for these highly disordered solvent molecules had been removed with the SQUEEZE routine implemented in PLATON.[3] The molar ratio of solvent molecules was calculated from the "squeezed" electron density; the given formula for Me$_3$-**2** and Me$_4$-**6** has been corrected for this solvent contribution. Structure figures were generated with DIAMOND-4.[4] All hydrogen atoms are calculated on idealized positions using the riding model. CCDC 1981552 (Me$_3$-**2**) and 1981553 (Me$_4$-**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://summary.ccdc.cam.ac.uk/structure-summary-form (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.uk). Tetrakis(triphenyl-phosphine)palladium was synthesised according to the literature.[5]

Electrochemical experiments

The electrochemical studies of the electrodes modified with **1**-**6** were carried out at room temperature by linear sweep voltammetry in 0.5 M aqueous sulfuric acid using an undivided electrochemical cell; the potential scan rate was 5 mV/s. The working electrode was a glassy carbon disk electrode with 3 mm^2 geometrical surface area. The auxiliary electrode was a platinum wire. An Ag/AgCl reference electrode (3.0 M KCl) was used, and nitrogen was used for deaeration of the solutions.

Preparation of the modified electrode

Compounds **1**-**6** were dissolved in toluene (concentration 7 mol·L^{-1}). The solution was spread on the surface of the electrode and then the electrode was dried.

Synthesis of organic compounds 1-6

Synthesis of triphenylamine derivative **1**,[6] anthracene derivative **3**[7] and tetraphenylethylene derivative **5**[8] was performed according to the literature.

The synthesis of compounds **2**, **4** and **6** was achieved by a Pd-catalyzed Suzuki-Miyaura coupling reaction between the brominated starting materials and [4-(*E*-3-methoxy-3-oxo-1-propen-1-yl)phenyl]boronic acid, followed by a base-catalyzed hydrolysis reaction. The final product was then obtained by saponification to obtain the corresponding carboxylic acids.

The acid *trans*-4-(2-carboxyethenyl)benzeneboronic acid was synthesized based on a known literature procedure.[9] The methyl ester, employed in the Pd-catalyzed Suzuki-Miyaura coupling reaction, [4-(*E*-3-methoxy-3-oxo-1-propen-1-yl)phenyl]boronic acid, was obtained by esterification with methanol.

Synthesis of compound **2**:

Tris(4-bromophenyl)amine was synthesized according to the literature.[10]

Tris(4-bromophenyl)amine (1.00 g, 0.002 mol), [4-(*E*-3-methoxy-3-oxo-1-propen-1-yl)phenyl]boronic acid (2.32 g, 0.011 mol, 4.5 eq.), tetrakis(triphenylphosphine)palladium (0.034 g, 0.03 mmol, 0.015 eq.), sodium carbonate (1.69 g, 0.016 mmol, 8 eq.) and 150 mL degassed dioxane were added to a 250 mL three-neck round bottom flask. The solution was refluxed for 72 h under nitrogen. After cooling to room temperature, the solvent was evaporated under vacuum and the remaining solid was dissolved in dichloromethane. This solution was extracted with water and the organic phase was separated and dried over $MgSO_4$. Pale yellow crystals of the methyl ester of **2** (Me_3-**2**) suitable for single crystal X-ray diffraction were obtained (1.35 g, yield: 90%). Details about the crystal structure determination of Me_3-**2** are given in Table S1. ^1H NMR ($CDCl_3$), δ (ppm): 3.83 (s, 9H, Me), 6.43 (d, *J* = 16.0 Hz, 3H, vinyl), 7.22 (d, *J* = 8.4, 6H, arom. CH), 7.52 (d, *J* = 8.2, 6H, arom. CH), 7.58-7.61 (m, 12H, arom CH), 7.73 (d, *J* = 16.0 Hz, 3H, vinyl). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ (ppm): 51.9 (CH_3), 117.5 (vinyl C), 124.4 (arom. C), 124.7 (arom. C), 125.5 (arom. C), 127.1 (arom. C), 127.5 (arom. C), 128.1 (arom. C), 128.8 (arom. C), 132.6 (arom. C), 144.5 (vinyl. C), 167.6 (vinyl C). Anal. Calc. (%) for $C_{53}H_{47}NO_6$ (one molecule of toluene included): C, 80.18; H, 5.97, N, 1.76; found (%) C, 80.37; H, 5.71; N, 1.72.

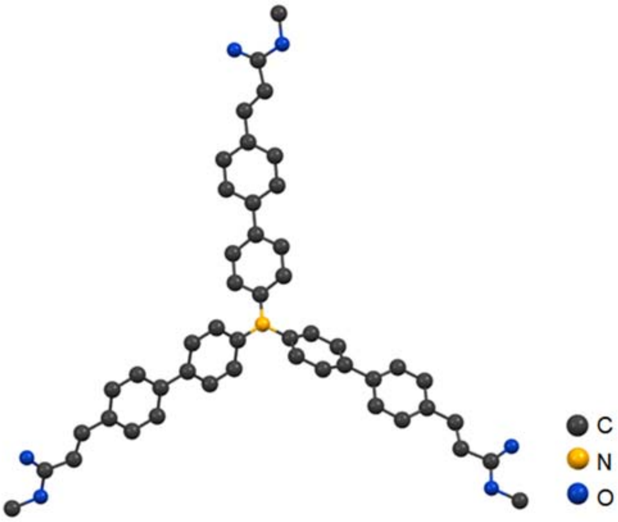
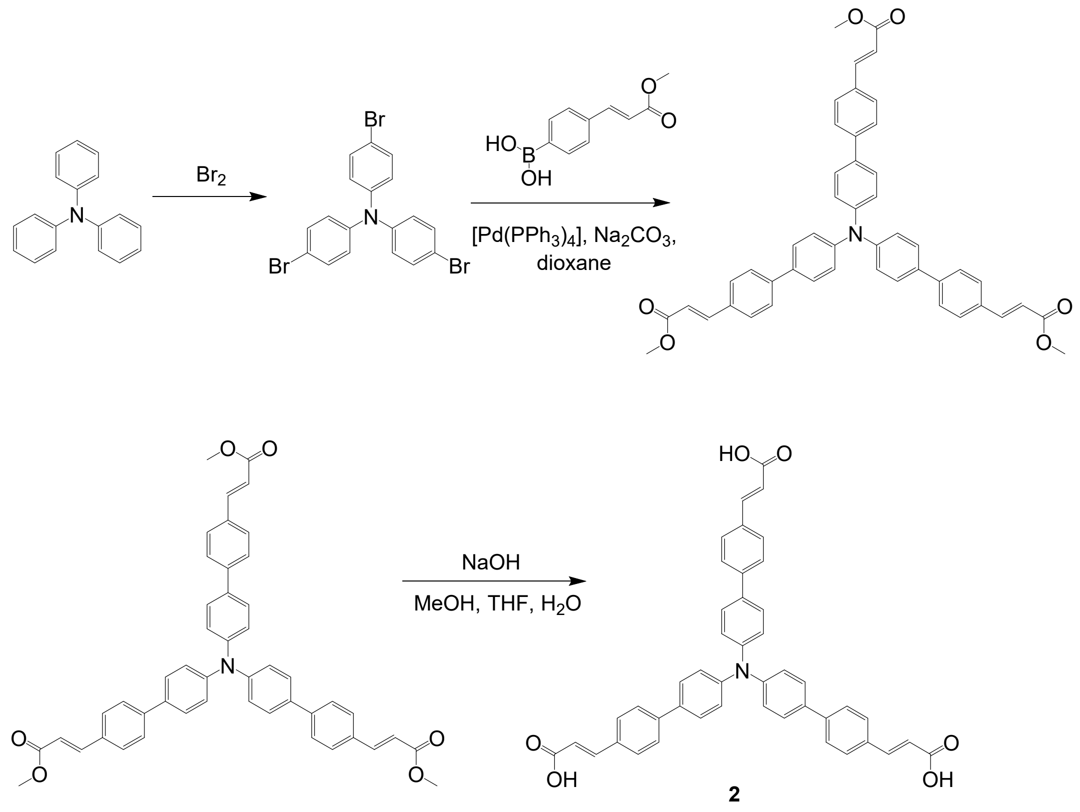


Figure S1. Molecular structure of Me_3-**2**.

Table S1. Crystal data and structure refinement for Me$_3$-**2**.

Compound	Me$_3$-**2**
Molecular formula	$C_{48}H_{39}NO_6 \cdot 1.5$ toluene
Empirical formula	$C_{58.5}H_{51}NO_6$
Formula weight	864.00
Temperature [K]	130(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a [pm]	1505.94(3)
b [pm]	3136.80(6)
c [pm]	1002.29(3)
α [°]	90
β [°]	101.519(2)
γ [°]	90
Volume [nm^3]	4.6393(2)
Z	4
$\rho_{\text{(calc.)}}$ [Mg/m^3]	1.237
μ [mm^{-1}]	0.079
F(000)	1828
Crystal size [mm^3]	0.4 x 0.4 x 0.05
Θ_{min} - Θ_{max} [°]	1.895 - 25.350
Index ranges	$-18 \leq h \leq 18$, $-37 \leq k \leq 37$, $-12 \leq l \leq 11$
Reflections collected	41669
Independent reflections [$R_{(int)}$]	8484 [0.0434]
Completeness (Θ [°])	100.0 % (25.24)
T_{Max} / T_{Min}	1 / 0.97877
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8484 / 12 / 518
Goodness-of-fit on F^2	1.030
Final R indices [$I>2\sigma(I)$]	R1 = 0.0549, wR2 = 0.1383
R indices (all data)	R1 = 0.0840, wR2 = 0.1558
Largest diff. peak and hole [e·Å^{-3}]	0.256 / -0.248
CCDC-Nr.	1981552



Scheme S1. Synthesis of compound **2**

Compound **2** was obtained by saponification of Me$_3$-**2** with sodium hydroxide (19 eq.) in THF, water and methanol (v/v/v = 1:1:1). The mixture was refluxed overnight. After removal of the organic layer, the aqueous phase was acidified with HCl (6 M) to yield a yellow precipitate (1.09 g, yield: 85%). ^{1}H NMR (d$_6$-DMSO), δ (ppm): 6.62 (d, *J* = 15.9 Hz, 3H, vinyl), 7.25 (d, *J* = 9.2 Hz, 6H, arom. H), 7.69 (d, 6H, arom. H), 7.74-7.75 (m, 12H, arom. H), 7.81 (d, *J* = 16.2 Hz, 3H, vinyl), 12.50 (s, br. 3H, COOH). ^{13}C{^{1}H} NMR (d$_6$-DMSO), δ (ppm): 116.5 (vinyl C), 123.2 (arom. C), 127.4 (arom. C), 128.3 (arom. C), 129.8 (arom. C), 135.1 (arom. C), 138.8 (arom. C), 140.6 (arom. C), 144.2 (arom. C), 144.9 (vinyl. C), 171.5 (COOH). M.p. 242-244 °C. Anal. Calc. (%) for $C_{45}H_{33}NO_6$: C, 79.05; H, 4.86, N, 2.05; found (%) C, 79.16; H, 5.07, N 1.89.

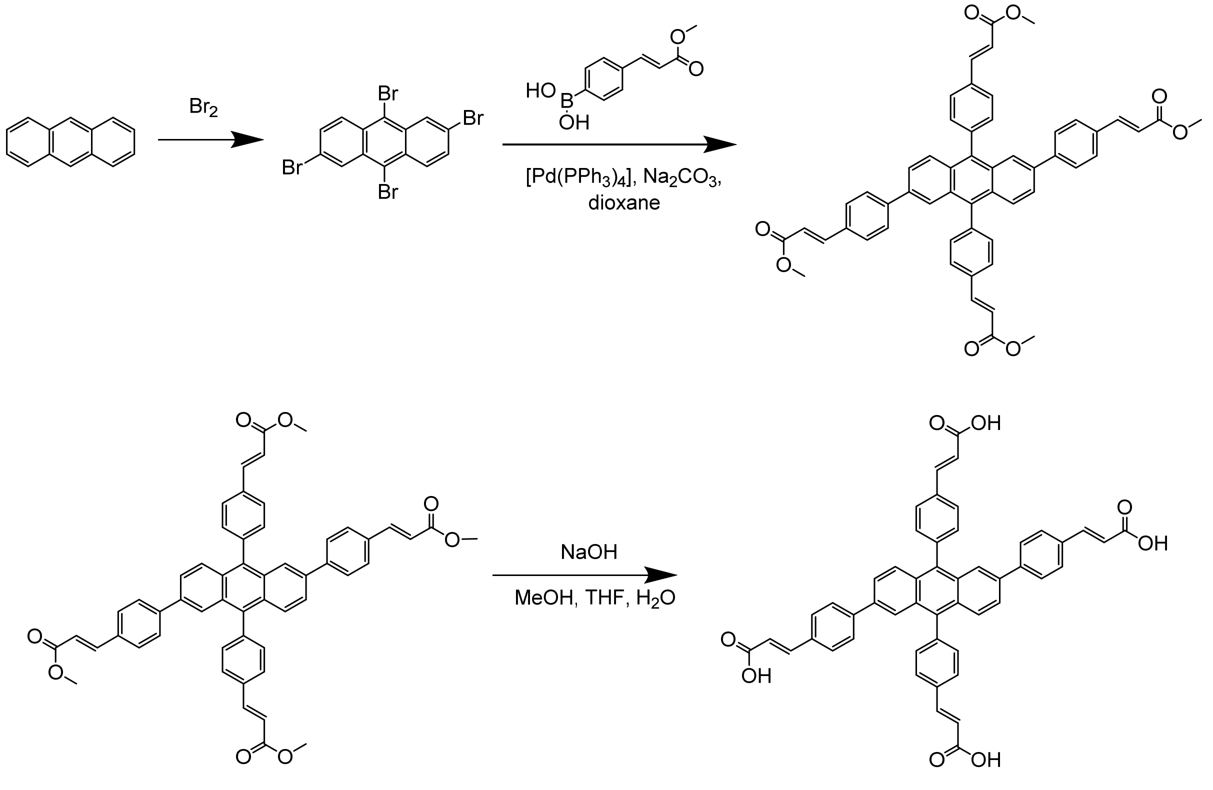
Synthesis of Compound **4**:

2,6,9,10-Tetrabromoanthracene was prepared according to the literature.[11]

2,6,9,10-Tetrabromoanthracene (1.00 g, 1.54 mmol, 1 eq.), [4-(*E*-3-methoxy-3-oxo-1-propen-1-yl)phenyl]boronic acid (1.72 g, 8.47 mmol, 5.5 eq.), tetrakis(triphenylphosphine)palladium (0.0266 g, 0.0231 mmol, 0.015 eq.), cesium fluoride (1.83 g, 1.23 mmol, 8 eq.) and 150 mL degassed dioxane were added to a 250 mL three-neck round bottom flask. The solution was refluxed for 72 h under nitrogen. After cooling to room temperature, the solvent was evaporated under vacuum and the remaining solid was dissolved in dichloromethane. This solution was extracted with water and the organic phase was separated and dried over $MgSO_4$. Afterwards, the solvent was reduced under low pressure and purification was achieved by column chromatography using *n*-hexane/ethyl acetate (8:1) with a rising gradient of ethyl acetate as eluent on silica. Yield of Me$_4$-**4**: 1.15 g (78%). ^{1}H NMR

($CDCl_3$), δ (ppm): 3.81 (s, 6H, CH_3), 3.92 (s, 6H, CH_3), 6.44 (d, *J* = 16.0 Hz, 2H, vinyl), 6.58 (d, *J* = 16.0 Hz, 2H, vinyl), 7.38-7.40 (m, 8H, arom. H), 7.45-7.48 (m, 4H, arom. H), 7.62 (s, 2H, arom. H), 7.68 (d, *J* = 16.0 Hz, 2H, vinyl), 7.84 (d, *J* = 16.0 Hz, 2H, vinyl), 7.90-7.94 (m, 8H, arom. H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$), δ (ppm): 51.2 (CH_3), 52.0 (CH_3), 115.2 (vinyl. C), 116.3 (vinyl. C), 124.5 (arom. C), 125.8 (arom. C), 126.9 (arom. C), 127.8 (arom. C), 128.4 (arom. C), 130.2 (arom. C), 131.8 (arom. C), 133.3 (arom. C), 134.1 (arom. C), 135.6 (arom. C), 137.2 (arom. C), 140.4 (arom. C), 143.6 (vinyl C), 144.5 (vinyl C) 166.5 (COO). Anal. Calc. (%) for $C_{54}H_{42}O_8$: C, 79.20; H, 5.17; found (%) C, 79.02; H, 5.31.

Compound **4** was obtained by saponification of Me_4-**4** with sodium hydroxide (26 eq.) in THF, water and methanol (v/v/v = 1:1:1). The mixture was refluxed overnight. After removal of the organic layer, the aqueous phase was acidified with HCl (6 M). The product precipitated as a bright yellow powder (0.87 g, yield: 68%). ^{1}H NMR (d_6-DMSO), δ (ppm): 6.27 (d, *J* = 16.0 Hz, 2H, vinyl), 6.64 (d, *J* = 16.0, 2H, vinyl), 7.33-7.37 (m, 8H, arom. H), 7.47-7.51 (m, 4H, arom. H), 7.59-7.67 (m, 10H, arom. H), 7.84 (d, *J* = 16.2 Hz, 2H, vinyl), 7.97 (d, *J* = 16.0 Hz, 2H, vinyl), COOH not observed. $^{13}C\{^{1}H\}$ NMR (d_6-DMSO), δ (ppm): 116.5 (vinyl C), 117.2 (vinyl C), 123.0 (arom. C), 125.4 (arom. C), 126.2 (arom. C), 127.4 (arom. C), 128.3 (arom. C), 129.8 (arom. C), 135.1 (arom. C), 138.8 (arom. C), 139.2 (arom C), 140.6 (arom. C), 144.2 (probably vinyl C), 144.9 (probably vinyl C), COOH not observed. M.p. 343-345 °C. Anal. Calc. (%) for $C_{50}H_{34}O_8$: C, 78.73; H, 4.49; found (%) C, 78.72; H, 4.38.



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Scheme S2. Synthesis of compound **4**

Synthesis of compound **6**:

Tetrakis(4-bromophenyl)ethene was synthesised according to the literature.[12]

Tetrakis(4-bromophenyl)ethene (1.00 g, 1.54 mmol), [4-(*E*-3-methoxy-3-oxo-1-propen-1-yl)phenyl]boronic acid (1.71 g, 8.47 mmol, 5.5 eq.), tetrakis(triphenylphosphine)palladium (0.0266 g, 0.0231 mmol, 0.015 eq.), cesium fluoride (1.83 g, 1.23 mmol, 8 eq.) and 150 mL degassed dioxane were added to a 250 mL three-neck round bottom flask. The solution was refluxed for 72 h under nitrogen. After cooling to room temperature, the solvent was evaporated under vacuum and the remaining solid was dissolved in dichloromethane. This solution was extracted with water and the organic phase was separated and dried over $MgSO_4$. Afterwards, the solvent was evaporated and the remaining solid was recrystallized from hot toluene. Yellow crystals suitable for single crystal X-ray diffraction were obtained (1.36 g, yield: 89%). Details about the crystal structure determination of the methyl ester of **6** (Me_4-**6**) is given in Table S2. ^1H NMR ($CDCl_3$), δ (ppm): 3.78 (s, 12H, CH_3), 6.42 (d, *J* = 16.0 Hz, 4H, vinyl), 7.28 (d, *J* = 8.4 Hz, 8H, arom. H), 7.48 (d, *J* = 8.6 Hz, 8H, arom. H), 7.53-7.59 (m, 16H, arom. H), 7.67 (d, *J* = 16.0 Hz, 4H, vinyl). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ (ppm): 51.6 (CH_3), 117.7 (vinyl C), 126.8 (arom. C), 126.4 (arom. C), 127.2 (arom. C), 128.6 (arom. C), 132.0 (arom. C), 133.3 (arom. C), 138.2 (arom C), 140.6 (arom. C), 142.3 (probably ethylene C),144.4 (vinyl C), 167.4 (COO). Anal. Calc. (%) for $C_{66}H_{52}O_8$: C, 81.46; H, 5.39; found (%) C, 81.77; H, 5.73.

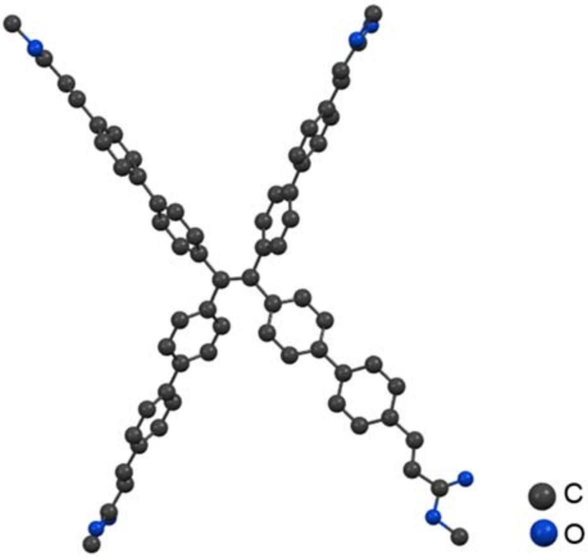


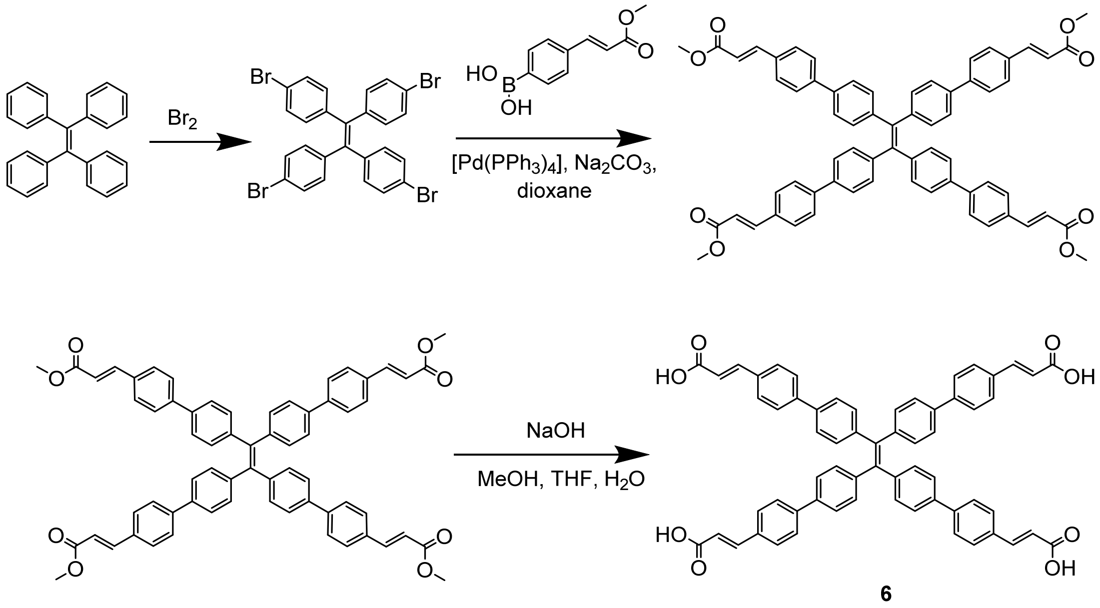
Figure S2. Molecular structure of Me_4-**6**.

Table S2. Crystal data and structure refinement for Me$_4$-**6.**

Compound	Me$_4$-**6**
Molecular formula	$C_{66}H_{52}O_8$·3 Toluene
Empirical formula	$C_{87}H_{76}O_8$
Formula weight	1249.47
Temperature [K]	130(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a [pm]	1072.86(4)
b [pm]	1642.91(7)
c [pm]	1989.92(8)
α [°]	99.436(3)
β [°]	104.873(3)
γ [°]	92.275(3)
Volume [nm^3]	3.3318(2)
Z	2
ρ $_{\text{(calc.)}}$ [Mg/m^3]	1.245
μ [mm^{-1}]	0.079
F(000)	1324
Crystal size [mm^3]	0.2 x 0.2 x 0.1
Θ_{min} - Θ_{max} [°]	1.800 - 23.256
Index ranges	$-11 \le h \le 11$, $-18 \le k \le 13$, $-22 \le l \le 22$
Reflections collected	20915
Independent reflections [$R_{(int)}$]	9558 [0.0478]
Completeness (Θ [°])	99.9 % (23.26)
T_{Max} / T_{Min}	1 / 0.99415
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least squares on F^2
Data / restraints / parameters	9558 / 0 / 671
Goodness-of-fit on F^2	1.000
Final R indices [I>2σ(I)]	R1 = 0.0680, wR2 = 0.1604
R indices (all data)	R1 = 0.1543, wR2 = 0.1973
Largest diff. peak and hole [e·Å^{-3}]	0.245 / -0.183
CCDC Nr.	1981553

Compound **6** was obtained by saponification of Me$_4$-**6** with sodium hydroxide (26 eq.) in THF, water and methanol (v/v/v = 1:1:1). The mixture was refluxed overnight. After removal of the organic layer, the aqueous phase was acidified with HCl (6 M) to yield a pale yellow precipitate (1.20 g, yield: 90%). ^{1}H NMR (d$_6$-DMSO), δ (ppm): 6.56 (d, *J* = 16.4 Hz, 4H, vinyl), 7.16 (d, *J* = 8.3 Hz, 8H, arom. H), 7.52-7.60 (m, 8H, arom. H), 7.61 (d, *J* = 16.4 Hz, 4H, vinyl), 7.69-7.71 (m, 16H, arom. H), 12.47 (s, 4H, COOH). ^{13}C{^{1}H} NMR (d$_6$-DMSO), δ (ppm): 116.5 (vinyl C), 125.6

(arom. C), 125.8 (arom. C), 127.5 (arom. C), 128.0 (arom. C), 129.0 (arom. C), 130.0 (arom. C), 130.4 (arom. C), 131.6 (arom. C), 139.6 (probably ethylene C), 144.6 (vinyl C) 167.5 (COOH). M.p. 220-222 °C. Anal. Calc. (%) for $C_{62}H_{44}O_8$: C, 81.21; H, 4.84; found (%) C, 81.07; H, 4.90.



Scheme S3. Synthesis of compound **6**.

Photocatalysis

The photocatalytic experiments were conducted in a self-made apparatus. A TQ 150 mercury middle-pressure immersion lamp (150 W) was used as light source (Peschl Ultraviolet). The lamp was protected by a cooling jacket made from quartz glass and immersed into the catalyst suspension. The hydrogen, which was evolved during the reaction, was quantified using a HP 6890 Series gas chromatograph (GC, Hewlett Packard). The GC was equipped with a HayeSep column and the evolving hydrogen was quantified using a thermal conductivity detector. The evolving gases were pumped continuously through the GC. A sample was taken every 2.5 min for 2 h.

For each experiment, 40 mg of the organic carboxylic acids **1**-**6** were suspended in 380 mL water containing 10 vol.-% MeOH. 0.127 mL of a 20 mM $H_2[PtCl_6]$ solution were added to the suspension resulting in a 0.5 wt.-% deposition of elemental platinum nanoparticles on the surface of the organic material during the reaction.[13] The mixture was sonicated and connected with the apparatus described above. Prior to every experiment, the whole apparatus was purged with nitrogen for 10 min until the detected amount of oxygen was 0.00 %. During the experiments, the temperature was kept constant at 25 °C within ±0.5 °C.

Solid-state UV-vis Spectra

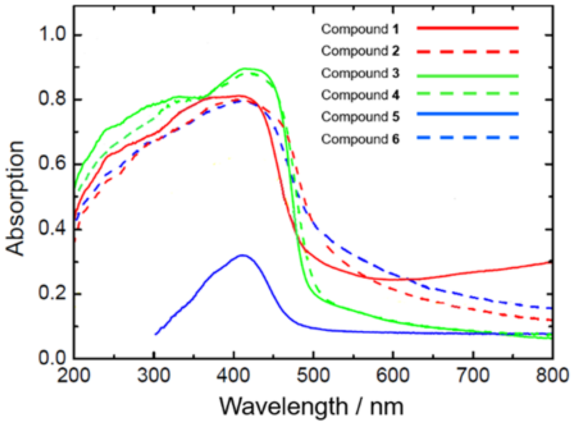


Figure S3. Solid-state UV-vis spectra of compounds **1**-**6**.

UV-Vis spectra in CH_2Cl_2

UV-Vis spectra were obtained with a Perkin-Elmer Lambda 900 spectrometer, in CH_2Cl_2 at room temperature. The concentration of compounds **1**-**6** was 10^{-7} M.

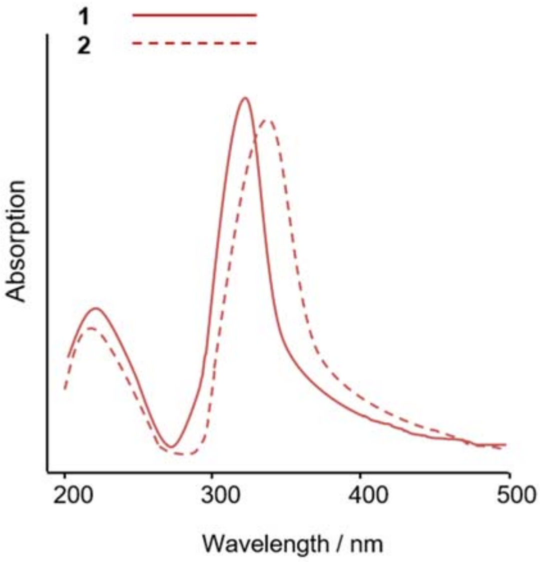


Figure S4. UV-Vis spectra of **1** and **2** in CH_2Cl_2.

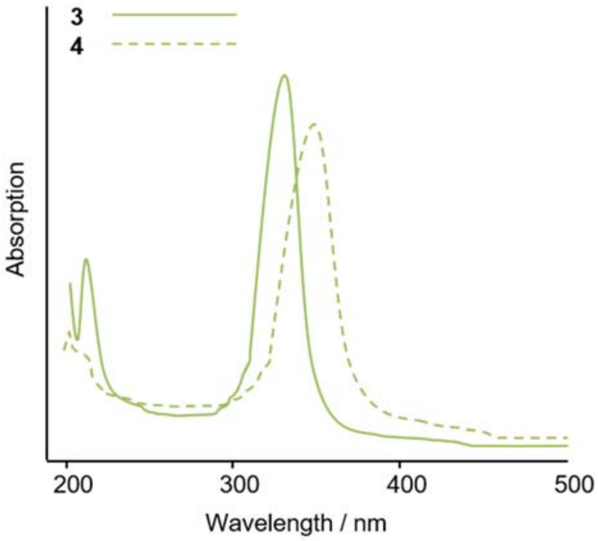


Figure S5. UV-Vis spectra of **3** and **4** in CH_2Cl_2.

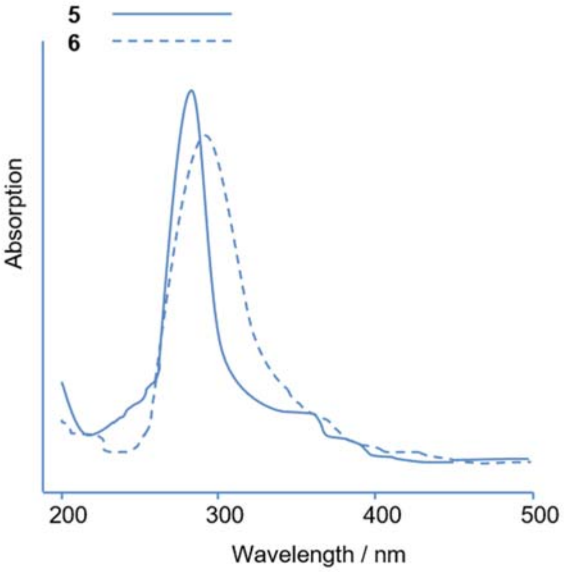


Figure S6. UV-Vis spectra of **5** and **6** in CH_2Cl_2.

Calculated UV-vis spectra

Geometries of compounds **1-6** were optimized using the CAM-B3LYP density functional and Def2TZVP basis set as implemented in Gaussian16.[14] Implicit dichloromethane solvent was applied using the Polarisable Continuum Model (PCM). In the case of compounds **2**, **4**, and **6** containing the vinyl groups, *cis* and *trans* isomers were optimized. The optimized geometries were then used to calculate the UV-Vis spectra. The lowest 10 states were employed in the TD-DFT calculation.

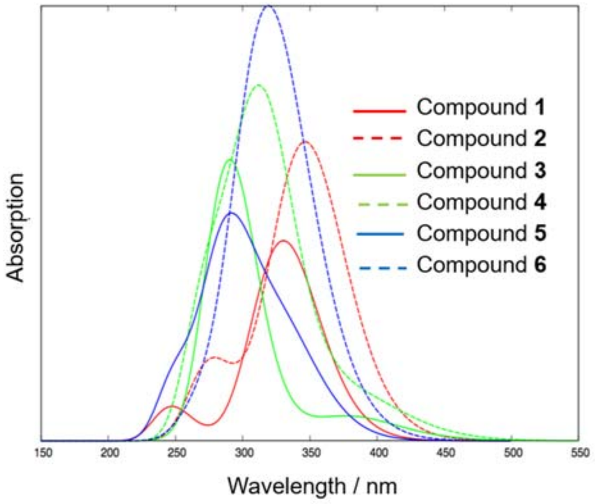


Figure S7. Calculated (CAM-B3LYP/Def2TZVP) UV-Vis spectra of **1-6** in CH_2Cl_2 (color code: **1** (solid red line), **2** dashed red line), **3** (solid green line), **4** dashed green line), **5** (solid blue line), **6** (dashed blue line).

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