

Pentacene to Octacene: The Limit of Fourfold TIPS-Ethynylation


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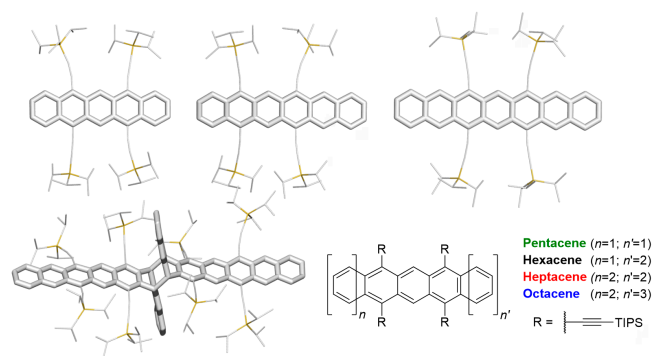
Abstract Soluble acenes beyond hexacene are rare. Their sensitivity complicates isolation, purification and application in devices. To increase the stability of acenes, functionalization with trialkylsilyl ethynyl substituents prevents [4 + 4] dimerization and oxidation. At the same time, such acenes are soluble and processible. Here we present the modular synthesis of fourfold tri-*iso*-propylsilyl ethynyl-ethynylated pentacenes to octacenes and investigate their optical and redox properties, frontier orbital positions (CV, density functional theory calculations) as well as their stability in solution (UV/vis, NMR spectroscopy). We also investigated their magnetic properties as a function of acene length. Pentacene, hexacene and heptacene are sufficiently stable to serve as semiconductors in thin-film transistors – the octacene rapidly decays to its butterfly dimer evidence by time-dependent NMR spectroscopy and crystal structure analysis.

Key words: acenes, heptacene, hexacene, octacene, pentacene, polycyclic aromatic hydrocarbons, steric shielding

Introduction

Acenes are prominent organic semiconductors.¹ Pentacene, a benchmark material for thin film transistors,² displays charge carrier mobilities up to 5–40 cm²/Vs. Hexacenes, heptacenes and longer acenes offer lower reorganization energies,³ predicted higher charge carrier mobilities⁴ and a narrower bandgap.⁵ Yet, these improved electronic properties come at the cost of reduced stability and solubility – a challenge for their synthesis and characterization.⁶

The loss of stability in the higher acenes is due to oxidation and cycloaddition reactions.⁷ In the case of pentacene, endoperoxide formation and dimerization are the main de-



composition pathways in solution.^{7b,8} Although the synthesis of longer acenes (up to dodecacene)⁹ has been achieved on surfaces or in matrices,¹⁰ stability – or their lack of solubility – is an issue, reflected by the low number of published examples of soluble hexacenes to nonacenes.¹¹

Triisopropylsilyl ethynylation in combination with arylation allowed Anthony et al. to prepare soluble nonacenes.^{11e} They are fully characterized but perhaps not stable enough to be processed as semiconductors in organic field-effect transistors.

Stabilizing larger acenes is imperative for processing, spectroscopic investigation and potential application.¹² Silylalkynylation improves the solubility and stability of long acenes. Endo-peroxide formation is reversible¹³ and bulky trialkylsilanes suppress dimerization.¹² Tri-*tert*-butylsilyl ethynyl or tri-*iso*-propylsilyl ethynyl (TIPS) groups stabilize hexacenes, and tris(trimethylsilyl)silyl ethynyl substituents are necessary to stabilize heptacenes.¹⁴ Additional substituents, aryl or trialkylsilyl ethynyl groups, must be placed along the zig-zag edges to increase their stability.^{11a,11c,11e,15}

To our knowledge, the most stable alkynylated hexacene **A** (Figure 1, one-dimensional π -stacking) and heptacene **B** (Figure 1, no π - π interactions in the solid state) decompose in solution under ambient conditions within a few days (hexacene: $t_{1/2}$ = 99 h; heptacene: $t_{1/2}$ = 110 h).^{11a,15} Here, we

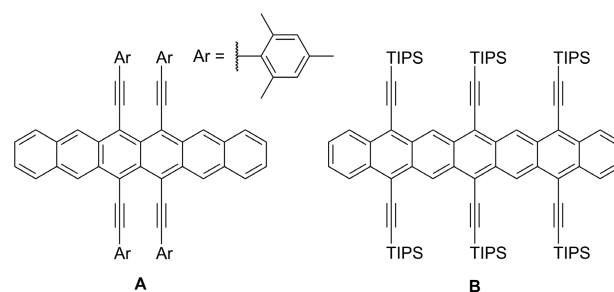
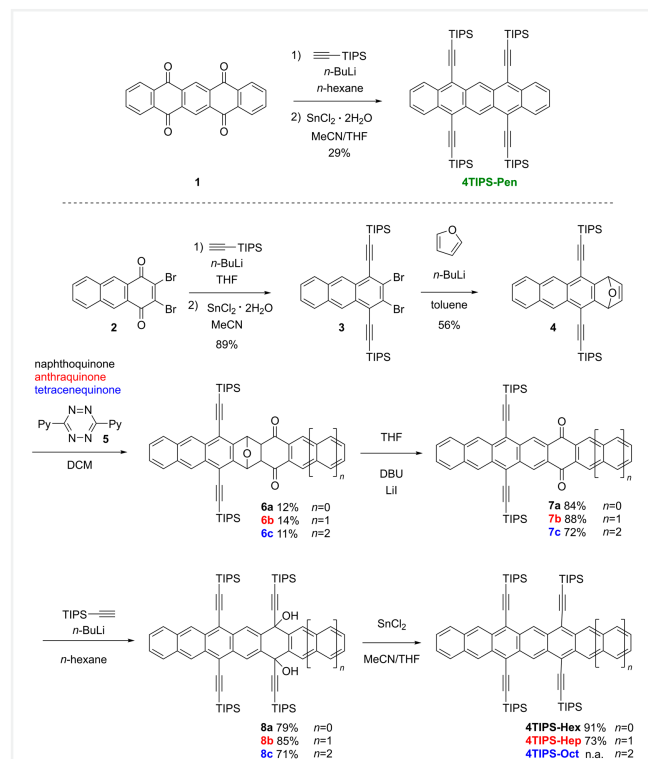


Figure 1 Structures of soluble hexacene **A**¹⁵ and heptacene **B**.^{11a}

explore the synthesis and the interplay of solid-state structure and stability of pentacene to octacene: We use fourfold TIPS-ethynylation around a central non-substituted benzene ring to investigate and compare a homologous series ranging from pentacene to octacene.

Results and Discussion

Commercially available pentacenetetraone **1** was reacted with an excess of lithiated TIPS-acetylene (100 equiv) in hexane to give tris- and tetrakis-alkynylated tri- or tetraols. These were reduced by $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in a mixture of acetonitrile and THF and **4TIPS-Pen** precipitates in 29% yield (Scheme 1, top) as analytically pure blue powder from the reaction mixture; other reduction byproducts remained in solution.



Scheme 1 Synthesis of the fourfold TIPS-ethynylated pentacene to octacene derivatives.

The synthesis of **4TIPS-Hex**, **4TIPS-Hep** and **4TIPS-Oct** was carried out according to that shown in Scheme 1, bottom. To prepare **4**, dibromoanthraquinone **2** was TIPS-ethynylation. Reaction with SnCl_2 afforded dibromoanthracene **3**. Generation of the aryne and Diels–Alder (DA) reaction with furan yielded epoxytetracene **4**. Naphtho-, anthra- or tetracenequinone, **4** and tetrazine **5** were reacted in a sequence of DA and retro-DA reactions to give **6a–c** in one

pot and as mixtures of stereoisomers, which were deoxygenated into **7a–c** with DBU and LiI. The double ethynylation of **7a–c** with lithiated TIPS acetylene (10 equiv) gave **8a–c**; reduction with SnCl_2 furnished **4TIPS-Hex** in 91% and **4TIPS-Hep** in 71%. The final products precipitated as dark, intensely colored solids, soluble in THF, toluene and DCM. **4TIPS-Hex** and **4TIPS-Hep** were stable for a month as solids under N_2 .

4TIPS-Oct decomposed rapidly in solution, even under N_2 in the dark. Attempts to purify **4TIPS-Oct** were unsuccessful. Crystallization (N_2 atmosphere) from hot pyridine furnished its head-to-head butterfly dimer (Figure 2), in which the unsubstituted anthrylene side of the octacene had reacted and the $\text{C}_{\text{sp}3}\text{--C}_{\text{sp}3}$ bonds, which link the former octacene backbones, are slightly elongated. A thermally induced cleavage of these bonds could not be observed (see SI, S34). The dimer contains two pentacene fragments and appears blue. Mass spectra of **4TIPS-Oct** were contaminated by oxygen adducts. We assume the *endo*-peroxide to also form on one of the unsubstituted inner rings.^{11e} Upon attempted isolation of the degradation product of **4TIPS-Oct**, further decomposition occurred during column chromatography. **4TIPS-Oct** was characterized in the presence of its decomposition- and by-products (UV/vis, mass spectrometry).

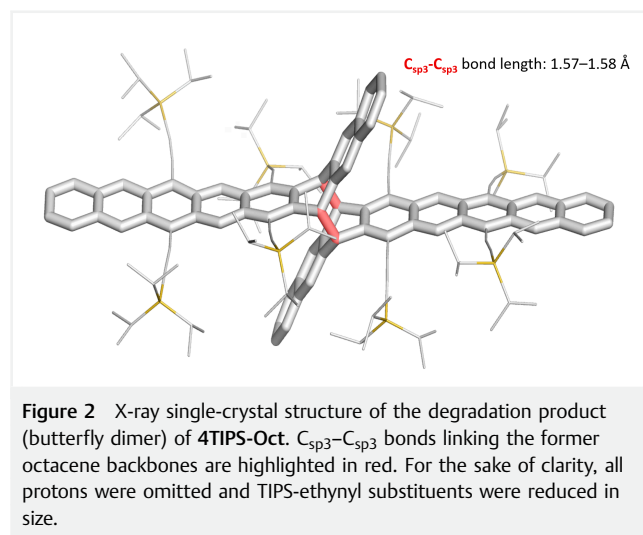


Figure 2 X-ray single-crystal structure of the degradation product (butterfly dimer) of **4TIPS-Oct**. $\text{C}_{\text{sp}3}\text{--C}_{\text{sp}3}$ bonds linking the former octacene backbones are highlighted in red. For the sake of clarity, all protons were omitted and TIPS-ethynyl substituents were reduced in size.

Single-crystal specimen of **4TIPS-Pen** – **4TIPS-Hep** were obtained by overlaying concentrated THF solutions with MeOH. The larger the acene backbone, the more difficult (and slower) the crystallization and the more amorphous the material. Crystals of **4TIPS-Pen** were blue, those of **4TIPS-Hex** and **4TIPS-Hep** green. The acene cores of **4TIPS-Pen** (19.6°) and **4TIPS-Hex** (18.5°) are twisted (torsion angle¹⁶ over the whole acene). In **4TIPS-Hep** the acene backbone deforms sigmoidally instead. The alkynyl substituents of **4TIPS-Pen** – **4TIPS-Hep** bend ($\text{C}_{\text{Ar}}\text{--C}_{\text{sp}}\text{--C}_{\text{sp}} \approx 170\text{--}174^\circ$

and $C_{sp}-C_{sp}-Si \approx 168-176^\circ$) as a consequence of the steric repulsion of the triisopropyl substituents. The torsion of the acene backbone^{11a} and alkyne bending is common for acenes with large proximal substituents.^{12,17}

The outermost C–C bonds of the zig-zag edges are shortened to 135 pm (Figure 3, green marked bonds). The robust bond length alternation of the outer rings coincides with reduced aromaticity and suggests that the Clar sextet is best placed on the middle benzene ring.¹⁸

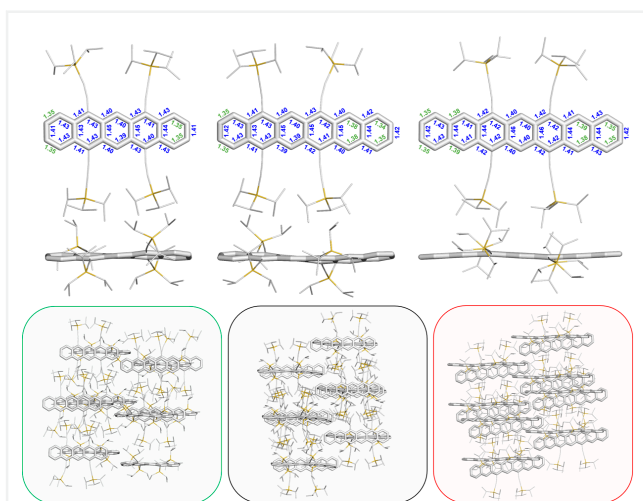


Figure 3 Top: X-ray single-crystal structures of **4TIPS-Pen**, **4TIPS-Hex** and **4TIPS-Hep** (top and side views) including bond lengths of the acene backbone (bond length $< 1.40 \text{ \AA}$ highlighted in green). For the sake of clarity, all protons were omitted and TIPS-ethynyl substituents were reduced in size. Bottom: Packing motifs of **4TIPS-Pen**, **4TIPS-Hex** and **4TIPS-Hep** determined by single-crystal structure analysis.

Similar to sixfold ethynylated heptacenes, the fourfold substituted acenes pack edge-to-face. The TIPS-ethynyl groups point towards the π -surface of neighboring acenes and suppress π – π interactions – even in the heptacene, the aspect ratio after going from six (**B**) to four (**4TIPS-Hep**) TIPS-ethynyl substituents is still unfavorable for a brick-wall-type arrangement.^{17a}

4TIPS-Pen–4TIPS-Oct absorb with acene-typical vibronically structured p-bands (λ_{\max} : **4TIPS-Pen**: 684 nm, **4TIPS-Hex**: 778 nm, **4TIPS-Hep**: 865 nm, **4TIPS-Oct**: 944 nm, Figure 4). Each added ring induces an ~ 80 – 90 nm red shift. The spectrum of **4TIPS-Oct** is superposed with that of its degradation products (band at 665 nm) testament to its rapid decomposition. The p-absorption band of **4TIPS-Hep** shows a shoulder at 907 nm and a peak at 1025 nm typical of heptacenes^{11a,11d,12} and indicates a partial diradical character¹⁸ – absent in the smaller acenes.

Solutions of the recrystallized acene derivatives (**4TIPS-Pen** to **4TIPS-Hep**, Table 1) were dissolved in DCM (c.a. $2.0 \times 10^{-6} \text{ M}$) and exposed to laboratory light and air at room temperature (rt) – UV/vis-spectra were recorded at suitable

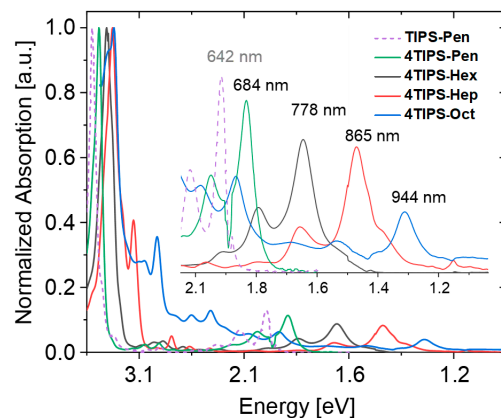


Figure 4 Normalized UV/vis absorption spectra of **TIPS-Pen** and **4TIPS-Pen–4TIPS-Oct** in DCM. Inset: Magnification of the p-band absorption maxima (also determined in nm).

Table 1 Absorption maxima and stabilities of **4TIPS-Pen–4TIPS-Oct**

Compound	λ_{\max} [nm]	λ_{\max} [eV]	$t_{1/2}$ [h]*
TIPS-Pen	642	1.93	52
4TIPS-Pen	684	1.81	75
4TIPS-Hex	778	1.59	68
4TIPS-Hep	865	1.43	22
4TIPS-Oct	944	1.31	1.5

*From decay of absorbance (toluene, ambient conditions) at λ_{\max} .

time intervals. For the stability measurement of **4TIPS-Oct**, we used the crude product, already contaminated by the degradation product at the beginning of the measurement. The larger acenes decompose more rapidly than the shorter ones: new absorption bands at shorter wavelengths (**4TIPS-Pen**: 356 nm, **4TIPS-Hex**: 427 nm, **4TIPS-Hep**: 428 nm, **4TIPS-Oct**: 665 nm) emerged while the p-bands lost intensity (see SI, Figure S33). The degradation product of **4TIPS-Oct** contains a pentacene fragment (cf. Figure 2) and those of **4TIPS-Hex**, **4TIPS-Hep** anthracene and **4TIPS-Pen** naphthalene subunits. As solids, **4TIPS-Pen–4TIPS-Hep** can be stored for several weeks under inert gas in the dark. Light is essential for decomposition – in the dark, solutions of the acenes were more stable (except for **4TIPS-Oct**).

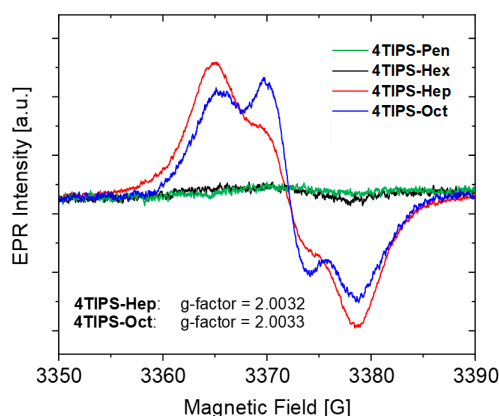
Steric shielding in **4TIPS-Pen**, **4TIPS-Hex** and **4TIPS-Hep** reduces degradation compared to their doubly silyl-ethynylated counterparts ($t_{1/2} \ll 24 \text{ h}$).^{11b,12,14} **4TIPS-Hex** ($t_{1/2} = 68 \text{ h}$) was more stable under these conditions than the shorter **TIPS-Pen** ($t_{1/2} = 52 \text{ h}$, see SI Section 2.2). Compared to sixfold TIPS-ethynylated heptacene **B**, **4TIPS-Hep** is less stable ($t_{1/2}$: 38 h vs. 22 h) – a consequence of the oxidation-sensitive central ring of **4TIPS-Hep**. Yet **4TIPS-Hep** is one of the most stable heptacenes to date.

Table 2 Photophysical and calculated properties of 4TIPS-Pen, 4TIPS-Hex, 4TIPS-Hep and 4TIPS-Oct

Compound	λ_{onset} [nm] ^[a]	$E_{\text{gap, opt}}$ [eV] ^[b]	E_{red1} [eV] ^[c]	E_{ox1} [eV] ^[c]	$E_{\text{gap, CV}}$ [eV] ^[d]	EA_{CV} [eV] ^[e]	IP_{CV} [eV] ^[f]	$E_{\text{gap, DFT}}$ [eV] ^[g]
4TIPS-Pen	710	1.75	-1.37	0.44	1.81	-3.73	-5.48	1.79
4TIPS-Hex	820	1.51	-1.31	0.26	1.57	-3.79	-5.30	1.48
4TIPS-Hep	950	1.31	-1.15	0.18	1.33	-3.95	-5.25	1.24
4TIPS-Oct	997	1.24	-1.14	0.08	1.22	-3.96	-5.20	1.05

[a] Onset of the lowest energy absorption maxima in DCM; [b] optical gap calculated by λ_{onset} ; [c] first reduction and oxidation potentials measured by CV in DCM using Bu_4NPF_6 as electrolyte vs. Fc/Fc^+ as internal standard (-5.1 eV^{21} at 0.2 Vs^{-1} ; [d] estimated by $E_{\text{gap, CV}} = E_{\text{ox1}} - E_{\text{red1}}$; [e] electron affinities estimated from first reduction potentials ($EA_{\text{CV}} = 5.10 \text{ eV} - E_{\text{red1}}$); [f] estimated using the approximation: $IP_{\text{CV}} = EA_{\text{CV}} - E_{\text{gap, opt.}}$; [g] $E_{\text{gap, DFT}}$ obtained from DFT calculations (Spartan'20, B3LYP/6-31 G*), TMS groups were used to approximate TIPS substituents.

According to the literature, higher acenes are diradical (oid)s.^{11a,11c,11e,18–19} A solution of **4TIPS-Hep** (and the crude **4TIPS-Oct**, see SI, S40) in DCM generated a weak, unresolved electron paramagnetic resonance (EPR) signal with a g-factor of 2.0032 (g-factor of 2.0033 for **4TIPS-Oct**). Pentacene and hexacene are both EPR silent (Figure 5). In the ^1H NMR spectrum of **4TIPS-Hep**, the signals are broadened at room temperature (SI), additional proof for the diradicaloid nature of higher acenes.

**Figure 5** EPR spectra of 4TIPS-Pen, 4TIPS-Hex, 4TIPS-Hep and crude 4TIPS-Oct in DCM at room temperature.

CV of **4TIPS-Pen–4TIPS-Oct** (ferrocene internal standard, Table 2) gives electrochemical gaps matching the optical gaps (**4TIPS-Pen**: 1.75 eV, **4TIPS-Hex**: 1.51 eV, **4TIPS-Hep**: 1.31 eV, **4TIPS-Oct**: 1.24 eV). CV of **4TIPS-Oct** was performed with freshly prepared material.²⁰ The computed HOMO–LUMO gaps for **4TIPS-Pen–4TIPS-Oct** (B3LYP/6-31 G*) agree with the experimentally determined gaps ($E_{\text{gap, DFT}}$: **4TIPS-Pen**: 1.79 eV, **4TIPS-Hex**: 1.48 eV, **4TIPS-Hep**: 1.24 eV, **4TIPS-Oct**: 1.05 eV).

To demonstrate the processability, **4TIPS-Pen** to **4TIPS-Hep** were used in tc/bg field effect transistors – with gold

as contact electrodes and a SAM modified dielectric.²² Thin films were obtained by drop-casting out of DCM (see SI). The average mobility increases with the size of the acene backbone. Hole mobilities of $\mu_{\text{p-ave}} = 2.4 \times 10^{-4} \text{ cm}^2/(\text{Vs})$ were measured for **4TIPS-Pen**. The hexacene and heptacene derivatives showed ambipolar behavior with almost balanced mobilities (see Table 3) of up to $0.023 \text{ cm}^2/\text{Vs}$ – each annealed benzene ring increases the average mobility by an order of magnitude.

Table 3 Average charge transfer mobilities of 4TIPS-Pen, 4TIPS-Hex and 4TIPS-Hep

Compound	$\mu_{\text{p-ave}}$ [$\text{cm}^2/(\text{Vs})$]	$\mu_{\text{n-ave}}$ [$\text{cm}^2/(\text{Vs})$]
4TIPS-Pen	$(2.4 \pm 0.8) \times 10^{-4}$	–
4TIPS-Hex	$(2.6 \pm 0.6) \times 10^{-3}$	$(1.0 \pm 0.5) \times 10^{-3}$
4TIPS-Hep	$(2.3 \pm 0.7) \times 10^{-2}$	$(1.2 \pm 0.4) \times 10^{-2}$

Conclusions

To conclude, we prepared a series of acenes ranging from pentacene to octacene. With increasing length, the optical gap decreases, while ionization potential and electron affinity (density functional theory, CV) are reduced. Pentacene to heptacene are well stabilized by four TIPS-ethynyl groups, but the octacene dimerizes to its butterfly adduct – dimerization (and oxidation) is fast at room temperature. The homologous series of acenes allowed for the first time to investigate the diradical character at RT as a function of acene length. **4TIPS-Hep** displays some diradical character at room temperature. **4TIPS-Pen–4TIPS-Hep** are sufficiently stable for device applications in thin film transistors.

Experimental Section

All reagents were obtained from commercial suppliers and were used without further purification if not otherwise stated. Anhydrous solvents were dispensed from the solvent purification system MBRAUN MB SPS 800. Deuterated sol-

vents were bought from MERCK (Darmstadt, Germany) or DEUTERO GmbH (Kastellaun, Germany). All reactions requiring exclusion of oxygen and moisture were carried out in heat-gun dried glassware under a dry and oxygen-free nitrogen or argon atmosphere using Schlenk and glovebox techniques. Column chromatography was performed using silica gel (SiO₂, pore size 60 Å, particle size 40–63 µm) manufactured by SIGMA ALDRICH. Melting points were determined in open glass capillaries on a Melting Point Apparatus MEL-TEMP (Electrothermal, Rochford, UK) and are uncorrected. X-ray single-crystal structure analyses of **4TIPS-Pen**, **4TIPS-Hex**, **4TIPS-Hep** and the dimer of **4TIPS-Oct** were measured on a STOE Stadivari CCD area detector diffractometer. NMR spectra were recorded on Bruker Avance III spectrometers using the specified frequency. HRMS spectra were obtained by (matrix-assisted) laser desorption/ionization (LDI/MALDI) using DCTB as matrix, electrospray ionisation or direct analysis in real time experiments. IR spectra of the powdery analytes were recorded on a Jasco FT/IR-4100 spectrometer. CV measurements were performed on a VersaSTAT 3 potentiostat by Princeton Applied Research in DCM using Bu₄NPF₆ as the electrolyte, Pt as the working electrode, Pt/Ti wire as the counter electrode, silver wire as the reference electrode and Fc/Fc⁺ as the internal standard. UV/vis spectra were recorded on a JASCO UV-VIS V-660 spectrometer using HELIMA ANALYTICS precision cells (10 mm, type 111-QS) under ambient conditions in non-degassed toluene at room temperature.

For detailed experimental procedure and characterization, please refer to the Supporting Information.

Funding Information

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Supporting Information

Supporting Information for this article is available online at <https://doi.org/10.1055/a-2241-0243>.

Primary Data

Compound characterization data are available through heidata, the institutional research data repository of Heidelberg University, under <https://doi.org/10.11588/data/DDJFGS>.

Conflict of Interest

The authors declare no conflict of interest.

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