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<td>density functional theory, TCNE cycloaddition, polycyclic aromatic hydrocarbon, donor-acceptor, pentacene</td>
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Synthesis, physical properties, and chemistry of donor/acceptor substituted pentacenes

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† Dedicated to Professor Reginald (Reg) Mitchell, with thanks for his support and collegiality through the years – thanks Reg!

Abstract. Pentacenes bearing electron donating and/or withdrawing groups, namely methoxy, dialkylamino-, and nitroaryl moieties, are synthesized to afford polarized pentacenes. The optical, electrochemical, and chemical properties of these derivatives are explored. The cycloaddition reaction of selective derivatives with tetracyanoethylene (TCNE) is explored, and the experimental results are rationalized on the basis calculations using density functional theory (DFT). X-ray crystallographic data provides insight molecular structure and intermolecular interactions present in the solid-state.

Keywords. pentacene • donor-acceptor • acene • polycyclic aromatic hydrocarbon • TCNE cycloaddition • density functional theory
**Introduction.** Structural variation is used to modify HOMO–LUMO energies, band gaps, solid-state packing, and numerous other structure-related properties in optoelectronic chromophores.\(^1,2,3,4\) To this end, the stepwise assembly of pentacenes has afforded structures with unusual and potentially useful structures.\(^5,6,7,8\) The functionalization of pentacene is typically achieved via two general approaches, placement of desired groups at the pro-cata positions (particularly the 2,3,9,10-positions, blue spheres in Figure 1) or at the peri-positions (particularly the 6,13-positions, red spheres in Figure 1). For example, pro-cata functionalization can be achieved with alkoxy,\(^9\) alkyl,\(^10\) alkynyl,\(^11\) aryl,\(^12\) carboxyl,\(^10a–b,13\) silyl,\(^14\) halo,\(^15\) and cyano\(^16\) groups. Functionalization of the 6,13-positions have been realized with alkyl,\(^17\) silylthynyl,\(^18\) aryl,\(^19\) arylethynyl,\(^20\) thioalkyl,\(^21\) cyano,\(^22\) trifluoromethyl,\(^23\) and Pt-acetylide\(^24\) groups, commonly via a 6,13-pentacenequinone precursor. The fusion of quinone,\(^25\) imide,\(^26\) or arene\(^27\) moieties to pentacene or the incorporation of heteroatoms into the chromophore can also be accomplished.\(^28\) These various substituents and substitution patterns can affect a wide range of properties including HOMO-LUMO energies, optical absorption/emission properties, solid-state packing, charge transport characteristics, and photostability.\(^1,2,19b,29\)

![Figure 1](https://mc06.manuscriptcentral.com/cjc-pubs)

**Figure 1.** Summary of common pentacene functionalization patterns: (a) Blue spheres illustrate the 2,3,9,10-positions (pro-cata positions) and (b) red spheres illustrate the 6,13-positions (peri-positions).

The formation of pentacenes with unsymmetrical 6,13-substitution can provide polarized
pentacenes with weak donor and acceptor substituents (e.g., 1d,e Scheme 1). Unfortunately, the synthetic protocol used in these cases, nucleophilic addition to pentacene quinone, does not tolerate strong electron-donating or -withdrawing groups such as the aniline and nitrophenyl moieties. This problem has now been solved through derivatization of the protected precursors 2a and 2b via palladium catalyzed Sonogashira cross-coupling reactions with aryl iodides. It should be emphasized that intermediates 2a,b and related structures provide powerful building blocks for a wide range of cross-coupling, cycloaddition, and coordination reactions as recently demonstrated in the synthesis of oligomeric pentacenes and inorganic complexes with functionalized pentacenes.

Scheme 1. Synthesis of 4a–e and 1a–c (this work) and structures of 1d,e (from ref. 30).

Synthesis of donor/acceptor pentacenes. The reaction of 2a,b with iodoaryl derivatives 3a–c afforded 4a–d. Aniline derivative 4a partially decomposed during chromatographic purification on silica gel, leading to a low isolated yield. Dimethylaniline substituted 4b was likewise unstable on silica gel, but could be isolated pure and in high yield via recrystallization (see SI for details). Nitrobenzene derivative 4c was, on the other hand,
stable to purification via column chromatography. Sn\textsuperscript{II}-mediated reductive aromatization of 4a–c provided 1a–c (a shorter reaction time was used for the synthesis of 1c to minimize the reduction of the nitro group).\textsuperscript{36}

![Scheme 2](image)

**Scheme 2.** Synthesis of donor-acceptor pentacene 6a and structure of diphenyl derivative 6b (see SI for the synthesis of 6b).

A push-pull pentacene was then targeted. This began with the conversion of 4d to 4e via reaction with TBAF at low temperature to avoid products resulting from fluorodenitration (Scheme 1).\textsuperscript{37} A Sonogashira reaction of 4e with 3a then installed the dialkylaniline group, affording 5 (Scheme 2). Compound 5 was also unstable to purification on silica gel. Thus, after aqueous workup, the crude product was aromatized without prior chromatographic purification to provide donor-acceptor pentacene 6a, which could be isolated pure in 62% yield via column chromatography and crystallization.

**Characterization of donor/acceptor pentacenes.** UV–vis spectroscopy in CH\textsubscript{2}Cl\textsubscript{2} reveals $\lambda_{\text{max}}$ is moderately influenced by substitution changes in compounds 1a–e and 6a (Figures 2 and 3).\textsuperscript{38} Parent compound 1e (R = H) has $\lambda_{\text{max}} = 652$ nm, and this absorption is red-shifted via incorporation of increasingly electron donating groups to 655 nm (1d, R = OMe), 668 nm (1b, R = NMe\textsubscript{2}), and 674 nm (1a, R = Nn-Hex\textsubscript{2}). Appending a nitroaryl group gives $\lambda_{\text{max}} = 666$ nm for 1c, nearly equal to that of donor substituted 1b. The most strongly polarized pentacene derivative
6a (density functional calculations predict a dipole moment of 13.7 Debye, see SI for details) shows the lowest energy $\lambda_{\text{max}}$ at 689 nm, noticeably red-shifted versus the parent chromophore 6b$^{20a,39}$ ($\lambda_{\text{max}}$ 660 nm) as well as derivatives 1a–d. The red-shift for 6a is most dramatic in the solid state (see Figure S5), where the UV–vis spectrum of a thin film shows $\lambda_{\text{max}} = 823$ nm, shifted by 134 nm to lower energy than that in solution. Donor/acceptor pentacenes 1a–c and 6a show no significant emission in CH$_2$Cl$_2$.

![UV–vis absorption spectra](image)

**Figure 2.** UV-vis absorption spectra of 1a–e in CH$_2$Cl$_2$; inset expansion of low-energy region of UV-vis absorption spectra.
Figure 3. UV-vis absorption spectra of 6a,b in CH₂Cl₂; inset expansion of low-energy region of UV-vis absorption spectra.

Table 1. Optoelectronic, electrochemical, and thermal properties of pentacenes 1a–e and 6a,b.

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<tr>
<th>Cmpd</th>
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<th>E_g^{electro} (CH₂Cl₂)</th>
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*Lowest energy absorption maximum. 
b Thin film drop cast from CH₂Cl₂. 
Red-shift for the longest wavelength absorption λ_max measured between the solid and solution states. 
As determined from UV–vis spectroscopy, see reference 40. 
Cyclic voltammetry performed in benzene/MeCN (3:1 v/v) with 0.1 M n-Bu₄NPF₆ as supporting electrolyte at a scan rate of 150
mV/s. Potentials are referenced to the ferrocene/ferroacenium (Fc/Fc⁺) couple used as an internal standard. Quasi-reversible event. Data not measured.

Cyclic voltammetry (CV) has been used as a complementary method to UV–vis spectroscopy to examine the electronic make up of donor/acceptor pentacenes (Table 1). The presence of the electron-donating aniline groups significantly raises the energy of the HOMO, as observed by lower oxidation potentials for 1a and 1b ($E_{ox} = 0.16$ and $0.18$ V, respectively) relative to parent compound 1e ($E_{ox} = 0.39$ V). Reduction of nitro derivative 1c, on the other hand, is observed at a lower potential ($–1.33$ V) than 1e ($E_{red} = 1.44$ V) and correlating with a lower LUMO level. For donor-acceptor 6a, $E_{ox1} = 0.18$ V is nearly identical to 1a and 1b, while $E_{red1} = –1.34$ V is analogous to that of 1c, showing that the aniline and nitro groups dictate the initial redox events of 6a.

**Figure 4.** Solid-state packing of (a) pentacene 1b viewed down the short molecular axis, (b) pentacene 1b viewed down the long molecular axis, and (c) pentacene 6a viewed down the long
molecular axis showing three C–H⋯π interactions. Solvent molecules and hydrogen atoms omitted in (a–b); carbon = gray, nitrogen = purple, oxygen = red, silicon = gold.

Trends for electrochemical HOMO–LUMO gap ($E_g^{\text{electro}}$) are reasonably consistent with that calculated from the UV–vis data ($E_g^{\text{opt}}$) for 1a–e and 6a,b varying only by ±0.05 eV. Comparing $E_g^{\text{electro}}$ values, those of 1d–e are the highest 1.80–1.83 eV, while a slightly lower value $E_g^{\text{electro}} = 1.77$ eV is found for nitro derivative 1c. Aniline derivatives 1a,b show a further lowering of $E_g^{\text{electro}}$ (1.63 eV and 1.66 eV, respectively), and the greatest effect is observed for donor-acceptor 6a with $E_g^{\text{electro}} = 1.52$ eV ($E_g^{\text{opt}}$ of 1.49 eV), confirming the ability to influence HOMO and LUMO levels through substitution.

X-ray crystallographic structures of compound 1b and 6a are shown in Figure 4. The packing of 1b•0.5CH$_2$Cl$_2$ shows a 1-D slipped π-stacking arrangement with about two benzene rings worth of overlap and an interplanar distance between pentacene moieties of 3.40 Å. The solid-state packing of 6a features centrosymmetric cofacial dimeric pairs with interplanar distance between pentacenes of 3.46 Å. Although no long-range cofacial π-stacking is present, a number of C–H⋯π interactions seem to guide the long-range arrangement of 6a. The C–H bonds from the electron deficient nitroaryl moiety point into the faces of the adjacent electron rich aniline rings, which are likely the cause of the non-planar arrangement of the pendent aryl rings with respect to the pentacene framework. Furthermore, the hexyl chains from the aniline group appear to engage in C–H⋯π interactions with the aromatic core of the pentacene, with distances that range from 2.82 to 3.20 Å (see Figure S2). The nitroaryl group and the pentacene moiety show a 14.6° dihedral angle, while the dihedral angle between the aniline and the pentacene moieties is –27.6° (in the opposite direction).
**Reactions with TCNE.** Oligoacenes are known to undergo cycloaddition chemistry with a variety of cycloaddition partners including molecular oxygen, acetylene derivatives, arynes, fullerenes, as well as dimerization processes via [4+4] and others. The cycloaddition/cycloreversion of tetracyanoethylene (TCNE) with electron rich alkynes is a simple and mild reaction for the formation of optoelectronic materials with interesting properties. With the intent to form pentacene derivatives with an even stronger acceptor group, the reaction of TCNE with 1b was attempted toward the synthesis of 7b (Scheme 3). This reaction resulted in a mixture of products, from which the isolation of 7b was unsuccessful. The analogous reaction using 1d, on the other hand, gave the Diels–Alder adduct 8d, as confirmed by X-ray crystallography (Figure 5).

**Scheme 3.** Structure of pentacenes 7b and 7d and the synthesis of adduct 8d.
Figure 5. ORTEP representation of the X-ray crystallographic structure of 8d. Hydrogen atom not shown, and non-hydrogen atoms are represented by Gaussian ellipsoids at the 50% probability level.

In order to gain insight into the reactivity of pentacene 1d with TCNE and the origin for the preferential formation of the [4+2] product 7d over the [2+2]/retro[2+2] product 8d, we utilized density functional theory (DFT) calculations (see Figure 6, and the Supporting Information for results related to 1b). To reduce the computational cost, the triisopropylsilyl group in 1d (and its related structures) was replaced with a trimethylsilyl group (e.g., 1d'). Using B3LYP/6-31G(d), DFT calculations\textsuperscript{47} for both the [4+2] and [2+2] reactivity of 1d' with TCNE were performed to explore: (a) whether the overall reactions to 7d' and 8d' are exothermic, (b) which reaction pathway leads to the thermodynamically preferred product, (c) whether there are any intermediates that are exceedingly high in energy to be reasonably accessible, and (d) whether the relative energy of key transition state structures can provide insight into the origin for the experimental preference for the [4+2] over the [2+2] pathway.

The [2+2]/retro[2+2] pathway associated with 1d' and TCNE leads to two conformational isomers of product 7d', namely s-trans-7d' and s-cis-7d', each being exothermic relative to starting materials 1d' and TCNE by –32.0 and –31.3 kcal/mol, respectively. The formal
[2+2]-cycloaddition of TCNE with alkynes is known to proceed via stepwise mechanism\textsuperscript{48} and our DFT results are consistent with this (Figure 6). Relative to starting materials 1d’ and TCNE, transition state TS\textsuperscript{9d} is 31.4 kcal/mol higher in energy towards forming the first C–C bond to reach intermediate 10d (+28.0 kcal/mol) in the stepwise formal [2+2], en route to the exothermic cyclobutene intermediate 11d (−17.7 kcal/mol) and ultimately to products 7d’ via a retro[2+2] process. While the formal [2+2]/retro[2+2] pathway leads to the thermodynamic product, (s-trans-7d’), experimental results afford the [4+2]-product 8d, implying a Curtin-Hammett scenario must be operational. Namely, that rate determining step leading to 7d’ along the [2+2]/retro[2+2] pathway places an energy barrier of higher energy compared to the transition state leading to the [4+2] adduct (8d’). Indeed the electronic energy barrier for the TCNE-acene [4+2]-cycloaddition (TS\textsuperscript{12d} via 13d) leading to product 8d’ is 17.8 kcal/mol lower in energy compared to the first carbon-carbon bond forming transition state (TS\textsuperscript{9d}) in the stepwise TCNE-alkyne formal [2+2]-cycloaddition. This is the origin of the experimental preference to form product 8d over 7d. Analogous DFT analysis associated with dimethylamino substituted pentacene 1b reveals a similar scenario, with preference for [4+2] over [2+2] reactivity. Although, we were not able to locate the analogous transition state TS\textsuperscript{9b}, intermediate 10b is significantly higher in energy (+22.3 kcal/mol relative to starting materials 1b’ and TCNE) than the [4+2] transition state (TS\textsuperscript{12b}, +12.5 kcal/mol), thus indicating that [2+2] reactivity is also disfavoured in the case of substrate 1b (see Supporting Information for details).
Figure 6. DFT calculated energy profile using B3LYP/6-31G(d) for reaction of TCNE with pentacene 1b illustrating the origin of the preference for the [4+2] reactivity versus the formal [2+2]/retro[2+2] reactivity.
**Figure 7.** DFT calculated energy profile using B3LYP/6-31G(d) for reaction of TCNE with pentacene 4b' illustrating the origin of the preference for the formal [2+2]/retro[2+2] pathway versus the [4+2] pathway.
The sensitivity of the pentacene core to reactions with TCNE suggested the use of dehydropentacene precursor 4b in place of pentacene 1b (Scheme 4) towards achieving [2+2] reactivity with the alkyne instead of [4+2] reactivity with the pentacene to form product 14b’ instead of syn/anti-15, respectively. Examination of this hypothesis with DFT (structures 14–22, Figure 7) supports the feasibility for TCNE to preferentially react with the alkyne in a [2+2] manner instead of reacting with the acene in [4+2] fashion by using dehydropentacene 4b instead of pentacene 1b. Comparing the relevant transition states, the energy barrier associated with the [4+2] pathway (anti-TS17) is 6.5 kcal/mol higher than the highest energy barrier along the [2+2]/[4+2] pathway (TS20).

Experimentally, dehydropentacene 4b reacts cleanly with TCNE to provide an intensely red coloured product. While mass spectral analysis was consistent with formation of the expected product 14b, 1H and 13C NMR spectra of the product clearly shows two non-equivalent naphthyl moieties.39 This suggested that either an alternative product had formed, or that there is restricted or slow rotation on the NMR timescale with regard to the position of the aniline group relative to the two naphthyl moieties. Indeed, the later premise is supported by X-ray crystallography (Figure 8), which provided unambiguous proof of the structure of the isolated product and shows the aniline group located above one of the naphthyl moieties with contacts as short as 3.0–3.4 Å (carbons of aniline ring to plane of naphthyl ring). Unfortunately, attempted conversion of 14b to 23b under typical aromatization conditions using SnCl2•2H2O (with and without H2SO4), was not successful and attempts with forcing conditions (reflux) resulted in decomposition.
Scheme 4. Attempted synthesis of 23b from compound 14b.

Figure 8. ORTEP representation of the X-ray crystallographic structure of 14b. Hydrogen atom not shown, and non-hydrogen atoms are represented by Gaussian ellipsoids at the 50% probability level.

In summary, we have developed synthetic methodology that allows for appending strong electron-donating and -withdrawing groups on the pentacene framework and extension of this method to form a “push-pull” pentacene. The presence of a donor and/or acceptor has a significant effect on the electronic make-up of the acenes demonstrated by UV-vis and cyclic voltammetry analysis. This electronic influence also affects chemical reactivity, as
demonstrated by reactions of 1d and 4b with TCNE. The origin of the difference in reactivity towards TCNE with various pentacene derivatives is revealed using DFT calculations and provides design principles towards controlling [4+2] over [2+2] reactivity. This study contributes to paving the way to stronger donor-acceptor functionalized acenes for organic electronic applications which may be of use for improved solar cell performance based on singlet fission processes where charge transfer states are believed to play an important role.49

**Experimental section**

**General experimental methods**

Reagents were purchased in reagent grade from commercial suppliers and used without further purification. Compounds 1d,e, 2a,b, and 6b were synthesized via reported procedures. THF and benzene were distilled from sodium/benzophenone ketyl. CH2Cl2 and MeCN were distilled from CaH2. Anhydrous MgSO4 was used as the drying agent after aqueous work-up. Evaporation and concentration *in vacuo* was done at water-aspirator pressure. All reactions were performed in standard, dry glassware under an inert atmosphere of nitrogen or argon. Column chromatography: silica gel-60 (230–400 mesh). Thin Layer Chromatography (TLC): pre-coated plastic sheets covered with 0.20 mm silica gel with fluorescent indicator UV 254 nm; visualization by UV light or KMnO4 stain. Melting points are uncorrected. 1H- and 13C-NMR spectra were collected at 27 °C in CDCl3; solvent peaks (7.24 ppm for 1H and 77.0 ppm for 13C) as reference. Coupling constants are reported as observed (±0.5 Hz). UV-vis absorption spectra were acquired at rt using a Varian Cary 400 Scan Spectrometer; λmax in nm (ε in L•mol−1•cm−1). Emission spectra were recorded using Photon Technology International (PTI) MP1 Fluorescence system. For mass spectral analyses, low-resolution data are provided in cases when M+ is not the base peak; otherwise, only high-resolution data are provided. The samples for ESI
mass spectrometry were dissolved in ClCH₂CH₂Cl and made use of a 3:1 MeOH/toluene mixture as the carrier solvent. MALDI mass spectrometry used the matrix trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB).

Differential scanning calorimetry (DSC) measurements were measured on a Perkin Elmer Pyris 1 DSC instrument. Thermogravimetric analyses (TGA) were carried out on a Perkin Elmer Pyris 1 TGA instrument. All thermal analyses were carried out under a flow of nitrogen with a heating rate of 10 °C/min. Thermal decomposition temperature as measured by TGA (as sample weight loss) are reported as \( T_d \) in which the temperature listed corresponds to the intersection of the tangent lines of the baseline and the edge of the peak corresponding to the first significant weight loss, typically >5%. Melting points from DSC analysis are reported as the peak maxima, except in cases when the sample decomposed, in which case the onset temperature of the decomposition exothermic peak is reported, as well as the exothermic maxima corresponding to the decomposition.

Cyclic voltammetry experiments were done using a Bioanalytical Systems, Inc. (BASi) Epsilon Rotating-Disk Electrode (Model RDE-2). Data was analyzed by BASi Epsilon-EC Ver. 2.00.71–USB, BASi ComServer Ver. 1.03 on a PC computer. A three-electrode cell was used, using a platinum disk working electrode and a platinum wire counter electrode. Silver/silver ion (Ag in 0.1 M AgNO₃, 0.1 M n-Bu₄NPF₆ solution in MeCN) was used as a reference electrode. Ferrocene/ferrocinium (Fc/Fc⁺) was used as an internal standard. The potential values \( (E) \) were calculated using the following equation (except where otherwise noted): \( E = (E_{pc} + E_{pa})/2 \), where \( E_{pc} \) and \( E_{pa} \) correspond to the cathodic and anodic peak potentials, respectively. The potential values obtained in reference to Ag/Ag⁺ were converted to potentials vs. ferrocene/ferrocinium (Fc/Fc⁺). Solution cyclic voltammetry was performed in ca. 1 mM solution of pentacene.
derivatives in benzene/MeCN (3:1 v/v) containing 0.1 M n-Bu₄NPF₆ as supporting electrolyte at a scan rate of 150 mV•s⁻¹, except where noted otherwise. All solutions were deoxygenated with N₂ before each experiment and a blanket of N₂ was used over the solution during the experiment. The working electrode was polished with 0.05 µm alumina polish prior to each scan. Solutions of pentacenes 1a–e and 6b were analyzed with a scanning window of 1.0 V to –2.0 V (vs Ag/Ag⁺), while pentacene 6a was analyzed with a scanning window of 1.0 V to –2.2 V (vs Ag/Ag⁺).

X-ray data for 1b•0.5CH₂Cl₂ (CCDC 865682), 6a (CCDC 865683), 8d (CCDC 865684) and 14b (CCDC 865403) have been deposited at the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)122-333-6033. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via the Internet at www.ccdc.cam.ac.uk/data_request/cif using the CCDC numbers given above.

X-ray crystallographic data

Data for 1b. Crystals suitable for X-ray crystallographic analysis were obtained from a solution of 1b in CH₂Cl₂ which had been layered by acetone and allowed to slowly evaporate at 4 °C. X-ray data for 1b•0.5CH₂Cl₂: C₄₃H₄₃ClNSi•0.5CH₂Cl₂, Mᵣ = 644.34; crystal dimensions (mm) 0.39 × 0.19 × 0.08; monoclinic space group P2₁/c (No. 14); a = 9.2434(3) Å, b = 26.2155(8) Å, c = 14.8529(5) Å; β = 91.4551(4)°; V = 3598.0(2) Å³; Z = 4; ρcalcd = 1.189 g cm⁻³; μ = 0.171 mm⁻¹; λ = 0.71073 Å; T = –100 °C; 2θmax = 52.82°; total data collected = 28699; R₁ = 0.0423 [5794 observed reflections with Fo² ≥ 2σ(Fo²)]; wR₂ = 0.1122 for 426 variables, 0 restraints, and 7395 unique reflections; residual electron density = 0.551 and –0.568 e Å⁻³. (CCDC 865682).

Data for 6a. Crystals suitable for X-ray crystallographic analysis were obtained from a solution of 6a in CH₂Cl₂ which had been layered by acetone and allowed to slowly evaporate at 4 °C. X-ray data for 6a: C₅₀H₄₆N₂O₂, Mᵣ = 706.89; crystal dimensions (mm) 0.46 × 0.15 × 0.10; triclinic
space group P-1 (No. 2); \(a = 11.3590(8) \text{ Å}, b = 12.7835(8) \text{ Å}, c = 14.8035(10) \text{ Å}; \alpha = 74.2113(8)°, \beta = 72.9134(8)°, \gamma = 76.7681(8)°; V = 1951.1(2) \text{ Å}^3; Z = 2; \rho_{\text{calcd}} = 1.203 \text{ g cm}^{-3}; \mu = 0.073 \text{ mm}^{-1}; \lambda = 0.71073 \text{ Å}; T = \text{ -100 °C}; 2\theta_{\text{max}} = 51.56°; \) total data collected = 14731; \(R_1 = 0.0444 \) [5021 observed reflections with \(F_o^2 \geq 2\sigma(F_o^2)\)]; \(wR_2 = 0.1251 \) for 487 variables, 0 restraints, and 7477 unique reflections; residual electron density = 0.167 and \(-0.213 \text{ e Å}^{-3}\). (CCDC 865683).

**Data for 8d.** Crystals suitable for X-ray crystallographic analysis were obtained from a solution of 8d in CHCl\(_3\) which was allowed to slowly evaporate at 4 °C. X-ray data for 8d: \(C_{48}H_{40}N_4OSi, M_r = 716.93; \) crystal dimensions (mm) 0.40 \(\times\) 0.11 \(\times\) 0.07; monoclinic space group \(P2_1/c\) (No. 14); \(a = 15.9034(13) \text{ Å}, b = 12.3331(10) \text{ Å}, c = 20.8200(18) \text{ Å}; \beta = 103.3580(13)°; V = 3973.1(6) \text{ Å}^3; Z = 4; \rho_{\text{calcd}} = 1.199 \text{ g cm}^{-3}; \mu = 0.100 \text{ mm}^{-1}; \lambda = 0.71073 \text{ Å}; T = \text{ -100 °C}; 2\theta_{\text{max}} = 51.46°; \) total data collected = 29103; \(R_1 = 0.0467 \) [4791 observed reflections with \(F_o^2 \geq 2\sigma(F_o^2)\)]; \(wR_2 = 0.1118 \) for 487 variables, 0 restraints, and 7580 unique reflections; residual electron density = 0.207 and \(-0.305 \text{ e Å}^{-3}\). (CCDC 865684).

**Data for 14b.** Crystals suitable for X-ray crystallographic analysis were obtained from a solution of 14b in hexanes/CH\(_2\)Cl\(_2\) (3:1) which was allowed to slowly evaporate at 4 °C. X-ray data for 14b: \(C_{51}H_{49}N_5O_2Si, M_r = 792.04; \) crystal dimensions (mm) 0.42 \(\times\) 0.222 \(\times\) 0.11; triclinic space group \(P1\) (No. 2); \(a = 11.8561(6) \text{ Å}, b = 15.0323(10) \text{ Å}, c = 15.1075(10) \text{ Å}, \alpha = 115.327(7)°, \beta = 91.628(5)°, \gamma = 103.478(5)°, V = 2341.4(3) \text{ Å}^3; Z = 2; \rho_{\text{calcd}} = 1.123 \text{ g cm}^{-3}; \mu = 0.774 \text{ mm}^{-1}; T = 174(3) \text{ K}; 2\theta_{\text{max}} = 147.08°; \) total data collected = 16660; \(R_1 = 0.0607 \) [9138 observed reflections with \(F_o^2 \geq 2\sigma(F_o^2)\)]; \(wR_2 = 0.1873 \) for 566 variables, 9138 unique reflections, and 11 restraints; residual electron density = 0.59 and \(-0.44 \text{ e Å}^{-3}\). (CCDC 865403). Three disordered triisopropyl
groups were refined with the following occupancies: C4–C5, 30:70; C7–C8, 59:41; C10–C11, 51:49. In addition, a residual electron density pattern indicated a strongly disordered solvent molecule, likely CH$_2$Cl$_2$. All attempts to model and resolve this solvent molecule and the related disorder failed. Therefore finally the “solvent mask” option of OLEX2 was used to mask this region for refinement.$^{50}$

**Compound 1a**: To a solution of 4a (0.104 g, 0.129 mmol) in dry THF (10 mL) that had been deoxygenated by bubbling argon for 5 min was added SnCl$_2$·2H$_2$O (0.101 g, 0.448 mmol). The solution was stirred at rt for 5 h, poured onto a pad of silica gel, eluted with 1:1 CH$_2$Cl$_2$/hexanes, and the solvent was removed *in vacuo*. Column chromatography (silica gel, 3:2 CH$_2$Cl$_2$/hexanes) afforded 1a (0.080 g, 84%) as a deep blue solid. $R_f = 0.67$ (3:2 CH$_2$Cl$_2$/hexanes). UV–vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ ($\varepsilon$): 274 (sh, 21 300), 315 (181 000), 336 (sh, 21 700), 394 (11 000), 440 (2 660), 495 (3 580), 626 (sh, 12 200), 674 (18 400) nm. No significant emission in CH$_2$Cl$_2$. IR (CDCl$_3$ microscope): 3048 (w), 2955 (s), 2924 (s), 2863 (s), 2169 (s), 2120 (m), 1604 (s), 1526 (s) cm$^{-1}$.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 9.26 (broad s, 4H), 8.08–7.98 (m, 2H), 7.98–7.89 (m, 2H), 7.73 (d, $J = 8.7$ Hz, 2H), 7.44–7.32 (m, 4H), 6.72 (d, $J = 8.8$ Hz, 2H), 3.34 (t, $J = 7.5$ Hz, 4H), 1.70–1.58 (m, 4H), 1.44–1.20 (m, 33H), 0.98–0.89 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 148.4, 133.2, 132.2, 131.9, 130.8, 129.8, 128.7, 128.6, 126.3, 126.2, 125.8, 125.6, 119.7, 116.5, 111.4, 109.0, 107.2, 106.2, 105.1, 86.4, 51.1, 31.7, 27.3, 26.8, 22.7, 19.0, 14.1, 11.7. ESI HRMS $m/z$ calcd. for C$_{53}$H$_{64}$NSi ([M + H]$^+$) 742.4803, found 742.4787. TGA: $T_d \approx 410$ °C. DSC: decomposition, 177 °C (onset), 181 °C (peak).

**Compound 1b**: To a solution of 4b (0.121 g, 0.182 mmol) in dry THF (10 mL) that had been deoxygenated by bubbling argon for 5 min was added SnCl$_2$·2H$_2$O (0.204 g, 0.904 mmol). The solution was stirred at rt for 5 h, poured onto a pad of silica gel, eluted with 2:1 CH$_2$Cl$_2$/hexanes,
and the solvent was removed *in vacuo*. Column chromatography (silica gel, 2:1 CH₂Cl₂/hexanes) afforded 1b (0.097 g, 89%) as a deep blue solid. \( R_f = 0.80 \) (2:1 CH₂Cl₂/hexanes). UV-vis (CH₂Cl₂) \( \lambda_{\text{max}} (\epsilon) \): 275 (sh, 30 900), 314 (272 000), 389 (16 200), 440 (4 640), 481 (4 550), 619 (16 100), 668 (25 200) nm. No significant emission in CH₂Cl₂. IR (CH₂Cl₂ cast film): 3046 (w), 2941 (m), 2890 (w), 2863 (m), 2170 (m), 2120 (w), 1606 (s), 1525 (m), 1362 (m) cm\(^{-1}\). \(^1\)H NMR (500 MHz, CDCl₃): \( \delta \) 9.25 (s, 2H), 9.24 (s, 2H), 8.04–7.98 (m, 4H), 7.74 (d, \( J = 8.6 \) Hz, 2H), 7.42–7.35 (m, 4H), 6.76 (d, \( J = 8.7 \) Hz, 2H), 3.03 (s, 6H), 1.45–1.34 (m, 21H). \(^{13}\)C NMR (125 MHz, CDCl₃): \( \delta \) 150.4, 133.0, 132.2, 131.9, 130.8, 129.8, 128.7, 128.6, 126.3, 126.2, 125.8, 125.6, 119.5, 116.7, 111.9, 110.3, 106.8, 106.2, 105.1, 86.6, 40.2, 19.0, 11.7. \(^{13}\)C NMR (APT, 125 MHz, CDCl₃): \( \delta \) 150.4 (C), 133.0 (CH), 132.2 (C), 131.9 (C), 130.8 (C), 129.8 (C), 128.7 (CH), 128.6 (CH), 126.3 (CH), 126.2 (CH), 125.8 (CH), 125.6 (CH), 119.5 (C), 116.7 (C), 111.9 (CH), 110.3 (C), 106.8 (C), 106.2 (C), 105.1 (C), 86.6 (C), 40.2 (CH₃), 19.0 (CH₃), 11.7 (CH). ESI HRMS \( m/z \) calcd. for C₄₃H₄₄NSi ([M + H]^+) 602.3238, found 602.3221. TGA: \( T_d \approx 430 \) °C. DSC: decomposition, 162 °C (onset), 164 °C (peak).

**Compound 1c:** To a solution of 4c (0.105 g, 0.157 mmol) in dry THF (7 mL) that had been deoxygenated by bubbling N₂ for 5 min was added a solution of SnCl₂·2H₂O (0.082 g, 0.36 mmol) in THF (7 mL). The solution was stirred at rt for 3 h, poured onto a pad of silica gel, eluted with 1:1 hexanes/CH₂Cl₂, and the solvent was removed *in vacuo*. Column chromatography (silica gel, 1:1 hexanes/CH₂Cl₂) afforded 1c (0.053 g, 56%) as a green solid. \( R_f = 0.50 \) (1:1 hexanes/CH₂Cl₂). UV-vis (CH₂Cl₂) \( \lambda_{\text{max}} (\epsilon) \): 274 (29 700), 313 (255 000), 347 (14 600), 395 (14 600), 441 (7 090), 616 (14 400), 666 (22 900) nm. No significant emission in CH₂Cl₂. IR (CHCl₃, cast) 3048 (w), 2942 (m), 2890 (w), 2864 (m), 2185 (w), 2124 (w), 1589
(m), 1513 (m), 1337 (s) cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.94 (s, 2H), 8.54 (s, 2H), 8.09 (d, $J$ = 8.4 Hz, 2H), 7.75 (d, $J$ = 8.5 Hz, 2H), 7.62 (d, $J$ = 8.5 Hz, 2H), 7.46 (d, $J$ = 8.3 Hz, 2H), 7.32 (t, $J$ = 7.2 Hz, 2H), 7.26 (t, $J$ = 7.2 Hz, 2H), 1.46–1.36 (m, 21H). gCOSY NMR (500 MHz, CDCl$_3$): $\delta$ 8.94 $\leftrightarrow$ 7.75; 8.54 $\leftrightarrow$ 7.62; 8.09 $\leftrightarrow$ 8.94, 7.46 $\leftrightarrow$ 8.09, 7.75 $\leftrightarrow$ 8.94, 7.32 $\leftrightarrow$ 7.75; 7.62 $\leftrightarrow$ 8.54, 7.26 $\leftrightarrow$ 7.45, 8.09 $\leftrightarrow$ 7.26; 7.32 $\leftrightarrow$ 7.62. $^{13}$C NMR (500 MHz, CDCl$_3$): $\delta$ 146.6, 132.1, 131.9, 131.7, 130.1, 130.0, 129.8, 128.5, 128.3, 126.4, 126.1, 125.9, 125.0, 123.5, 119.6, 115.9, 107.8, 104.6, 101.9, 92.9, 19.0, 11.7. $^{13}$C NMR (APT, 125 MHz, CDCl$_3$): $\delta$ 146.6 (C), 132.1 (C), 131.9 (C), 131.7 (CH), 130.1 (C), 130.0 (C), 129.8 (C), 128.5 (CH), 128.3 (CH), 126.4 (CH), 126.1 (CH), 125.9 (CH), 125.0 (CH), 123.5 (CH), 119.6 (C), 115.9 (C), 107.8 (C), 104.6 (C), 101.9 (C), 92.9 (C), 19.0 (CH$_3$), 11.7 (CH). MALDI HRMS m/z calcd. for C$_{41}$H$_{37}$NO$_2$Si (M$^+$) 603.2588, found 603.2590. TGA: $T_d$ $\approx$ 330°C. DSC: decomposition, 197°C (onset), 225°C (peak).

**Compound 3a:** To a solution of BnEt$_3NICl$_2$^51$ (2.81 g, 7.203 mmol) in CHCl$_3$ (30 mL) and MeOH (15 mL) was added $N,N$-dihexylaniline (2.00 g, 7.65 mmol) and CaCO$_3$ (2.41 g, 24.1 mmol). The flask was wrapped in aluminum foil to protect from light and the reaction mixture was stirred for 48 h at rt. The solution was filtered through a pad of Celite with CH$_2$Cl$_2$ and the solvent was removed in vacuo. Column chromatography (silica gel, 10:1 hexanes/CH$_2$Cl$_2$) afforded 3a (2.51 g, 90%) as a clear yellow liquid. $R_f$ = 0.43 (10:1 CH$_2$Cl$_2$/hexanes). IR (CH$_2$Cl$_2$ cast film): 3086 (w), 2955 (s), 2928 (s), 2857 (m), 1589 (s), 1499 (s) cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.44 (d, $J$ = 8.6 Hz, 2H), 6.44 (d, $J$ = 8.9 Hz, 2H), 3.24 (t, $J$ = 7.7 Hz, 4H), 1.58 (quintet, $J$ = 6.7 Hz, 4H), 1.42–1.28 (m, 12H), 0.99–0.89 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 147.5, 137.5, 113.9, 75.3, 50.9, 31.7, 27.0, 26.7, 22.6, 14.0. $^{13}$C NMR (APT, 100 MHz, CDCl$_3$): $\delta$ 147.5 (C), 137.5 (CH), 113.9 (CH), 75.3 (C), 50.9 (CH$_2$), 31.7 (CH$_2$), 27.0 (CH$_2$), 26.7
(CH₂), 22.6 (CH₂), 14.0 (CH₃). EI MS m/z 387.1 (M⁺, 56), 316.1 ([M – C₅H₁₁]⁺, 100). EI HRMS m/z calcd. for C₁₉H₃₀IN (M⁺) 387.1423, found 387.1422.

**Compound 3b.** 4-Iodo-N,N-dimethylaniline was synthesized analogously to 3a (*vide supra*). Spectroscopic data of 3b was in agreement with that reported.⁵²b,d

**Compound 4a:** To a solution of 2a (0.288 g, 0.527 mmol) and 3a (0.331 g, 0.855 mmol) in THF (7 mL) and diisopropylamine (5.0 mL, 3.6 g, 35 mmol) which had been deoxygenated with argon for 10 min was added Pd(PPh₃)₄ (0.030 g, 0.026 mmol) and CuCl (0.005 g, 0.05 mmol) and the solution was further deoxygenated for 5 min. The solution was stirred for 20 h at 45–55 °C before being poured into satd. aq. NH₄Cl (200 mL). H₂O (100 mL) was added and the mixture was extracted with CH₂Cl₂ (80 mL, 50 mL). The organic phase was washed with 5% aq. NH₄Cl (200 mL), dried (MgSO₄), filtered, and the solvent removed *in vacuo*. Column chromatography (silica gel, 5:4 CH₂Cl₂/hexanes, column wrapped in aluminum foil to exclude light) afforded 4a (0.119 g, 28%) as a brown oil. Rᵣ = 0.38 (5:4 CH₂Cl₂/hexanes). IR (CH₂Cl₂ cast film): 3054 (w), 2931 (s), 2220 (m), 2169 (vw), 1607 (s), 1519 (s), 1081 (m), 1062 (m) cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ 8.71 (s, 2H), 8.54 (s, 2H), 8.02–7.97 (m, 2H), 7.97–7.92 (m, 2H), 7.59–7.51 (m, 4H), 7.23 (d, J = 9.0 Hz, 2H), 6.46 (d, J = 9.1 Hz, 2H), 3.21 (t, J = 7.7 Hz, 4H), 3.11 (s, 3H), 3.07 (s, 3H), 1.57–1.47 (m, 4H), 1.34–1.25 (m, 12H), 1.25–1.19 (m, 21H), 0.91–0.86 (m, 6H). ¹³C NMR (125 MHz, CDCl₃): δ 147.8, 134.8, 133.5, 133.4, 132.9, 132.8, 128.2, 128.0, 126.9, 126.6, 126.4, 110.9, 108.3, 106.3, 90.8, 88.6, 88.1, 75.7, 74.1, 52.1, 51.9, 50.9, 31.6, 27.1, 26.7, 22.6, 18.7, 14.0, 11.4 (one signal coincident or not observed). ¹³C NMR (APT, 125 MHz, CDCl₃): δ 147.8 (C), 134.8 (C), 133.5 (C), 133.4 (CH), 132.9 (C), 132.8 (CH), 128.2 (CH), 128.0 (CH), 126.9 (CH), 126.6 (CH), 126.4 (CH), 110.9 (CH), 108.3 (C), 106.3 (C), 90.8 (C), 88.6 (C), 88.1 (C), 75.7 (C), 74.1 (C), 52.1 (CH₃), 51.9 (CH₃), 50.9 (CH₂), 31.6 (CH₂), 27.1
(CH₂), 26.7 (CH₂), 22.6 (CH₂), 18.7 (CH₃), 14.0 (CH₃), 11.4 (CH) (one signal coincident or not observed). ESI MS m/z 804.5 ([M + H]⁺, 100), 772.5 ([M – OMe]⁺, 66). ESI HRMS m/z calcd. for C₅₅H₇₀NO₂Si ([M + H]⁺) 804.5170, found 804.5155.

**Compound 4b:** To a solution of 2a (0.285 g, 0.524 mmol) and 3b (0.152 g, 0.614 mmol) in THF (5 mL) and diisopropylamine (3 mL, 2 g, 0.2 mmol) which had been deoxygenated with argon for 10 min was added Pd(PPh₃)₄ (0.030 g, 0.026 mmol) and CuCl (0.005 g, 0.05 mmol) and the solution was further deoxygenated for 5 min. The solution was stirred for 20 h at rt before being poured into satd. aq. NH₄Cl (150 mL). H₂O (50 mL) was added and the mixture was extracted with CH₂Cl₂ (80 mL, 50 mL). The organic phase was washed with 5% aq. NH₄Cl (150 mL), satd. aq. NaCl (150 mL), dried (MgSO₄), filtered, and the solvent removed *in vacuo*. The residue was dissolved in a small amount of EtOAc (ca. 1 mL) to which MeOH (ca. 30 mL) was added. The solution was cooled to –78 °C, filtered, and the solid was washed with MeOH (3 × 5 mL) to afford 4b (0.254 g, 73%) as a white solid that is unstable to silica gel. IR (microscope): 3052 (w), 2942 (s), 2891 (m), 2864 (s), 2829 (w), 2816 (w), 2223 (m), 2164 (vw), 1609 (s) cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ 8.70 (s, 2H), 8.50 (s, 2H), 8.00–7.95 (m, 2H), 7.94–7.88 (m, 2H), 7.56–7.49 (m, 4H), 7.22 (d, J = 9.1 Hz, 2H), 6.50 (d, J = 9.1 Hz, 2H), 3.09 (s, 3H), 3.04 (s, 3H), 2.89 (s, 6H), 1.27–1.17 (m, 21H). ¹³C NMR (125 MHz, CDCl₃): δ 150.9, 134.7, 133.5, 133.3, 132.8, 128.21, 128.1, 126.9, 126.7, 126.5, 111.5, 109.8, 106.0, 91.3, 89.1, 87.6, 75.9, 73.9, 52.1, 51.9, 40.1, 18.8, 11.4 (one signal coincident or not observed). ESI MS m/z 686.3 ([M + Na]⁺, 3), 664.4 ([M + H]⁺, 2), 632.3 ([M – OMe]⁺, 100). ESI HRMS m/z calcd. for C₄₅H₄₀NO₂SiNa ([M + Na]⁺) 686.3425, found 686.3416.

**Compound 4c:** To a solution of 2a (0.410 g, 0.753 mmol) and 3c (0.171 g, 0.687 mmol) in THF (6 mL) and diisopropylamine (3 mL, 2 g, 0.2 mmol) which had been degassed for 10 min with
argon was added Pd(PPh$_3$)$_4$ (0.039 g, 0.34 mmol) and CuCl (0.011 g, 0.11 mmol). The reaction mixture was further deoxygenated with argon for an additional 2 min. The solution was stirred for 20 h at rt before being poured into satd. aq. NH$_4$Cl (150 mL). H$_2$O (50 mL) was added and the mixture was extracted with CH$_2$Cl$_2$ (80 mL, 50 mL). The organic phase was washed with 5% aq. NH$_4$Cl (150 mL), satd. aq. NaCl (150 mL), dried (MgSO$_4$), filtered, and the solvent removed in vacuo. Column chromatography (silica gel, CH$_2$Cl$_2$) afforded 4c (0.412 g, 90%) as an off white foamy solid. $R_f$ = 0.73 (CH$_2$Cl$_2$), 0.67 (2:1 hexanes/EtOAc), 0.24 (9:1 hexanes/EtOAc). IR (CH$_2$Cl$_2$ cast film): 3056 (w), 2943 (m), 2892 (w), 2865 (m), 2230 (vw), 2170 (vw), 1594 (m), 1520 (s), 1344 (s) cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.78 (s, 2H), 8.45 (s, 2H), 8.04 (d, $J$ = 8.2 Hz, 2H), 8.02–7.97 (m, 2H), 7.97–7.91 (m, 2H), 7.61–7.54 (m, 4H), 7.43 (d, $J$ = 8.2 Hz, 2H), 3.13 (s, 3H), 3.11 (s, 3H), 1.35–1.24 (m, 21H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 147.0, 133.6, 133.4, 133.0, 132.8, 132.3, 129.8, 128.5, 128.3, 128.1, 127.1, 126.92, 126.85, 123.2, 104.3, 97.2, 93.0, 83.5, 76.5, 73.3, 52.2, 51.9, 18.8, 11.4. $^{13}$C NMR (APT, 125 MHz, CDCl$_3$): $\delta$ 147.0 (C), 133.6 (C), 133.4 (C), 132.9 (C), 132.8 (C), 132.3 (CH), 129.8 (C), 128.5 (CH), 128.3 (CH), 128.1 (CH), 127.1 (CH), 126.92 (CH), 126.86 (CH), 123.2 (CH), 104.3 (C), 97.2 (C), 93.0 (C), 83.5 (C), 76.5 (C), 73.3 (C), 52.2 (CH$_3$), 52.0 (CH$_3$), 18.8 (CH$_3$), 11.4 (CH). MALDI HRMS $m/z$ calcd. for C$_{43}$H$_{43}$NO$_4$Si (M$^+$) 665.2956, found 665.2958. Anal. calcd. for C$_{43}$H$_{43}$NO$_4$Si: C, 77.56; H, 6.51; N, 2.10. Found: C, 77.34; H, 6.35; N, 2.21.

**Compound 4d:** To a solution of 2b (0.585 g, 0.993 mmol) and 3c (0.344 g, 1.38 mmol) in THF (7 mL) and diisopropylamine (5.0 mL, 3.6 g, 35 mmol) which had been deoxygenated for 10 min with argon was added Pd(PPh$_3$)$_4$ (0.030 g, 0.026 mmol) and CuCl (0.005 g, 0.05 mmol). The reaction mixture was further deoxygenated for an additional 2 min. The solution was stirred for 12 h at 40 °C before being poured into satd. aq. NH$_4$Cl (150 mL). H$_2$O (100 mL) was added and
the mixture was extracted with CH₂Cl₂ (80 mL, 50 mL). The organic phase was washed with 5% aq. NH₄Cl (150 mL), dried (MgSO₄), filtered, and the solvent removed in vacuo. Column chromatography (silica gel, 2:1 CH₂Cl₂/hexanes) afforded 4d (0.578 g, 82%) as an off white foamy solid. Rₜ = 0.65 (2:1 CH₂Cl₂/hexanes). IR (microscope): 3056 (w), 2952 (s), 2928 (m), 2896 (m), 2867 (m), 2230 (w), 2169 (w), 1595 (s), 1520 (s) cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ 8.70 (s, 2H), 8.44 (s, 2H), 8.03–7.96 (m, 2H), 7.96–7.90 (m, 2H), 7.59–7.54 (m, 4H), 7.42 (d, J = 9.1 Hz, 2H), 3.10 (s, 3H), 3.06 (s, 3H), 2.08 (n onet, J = 6.7 Hz, 3H), 1.11 (d, J = 6.6 Hz, 18H), 0.86 (d, J = 7.0 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃): δ 147.0, 133.6, 133.4, 133.0, 132.8, 129.8, 128.5, 128.2, 128.1, 127.1, 127.0, 123.3, 104.4, 97.2, 95.5, 83.5, 76.3, 73.3, 52.2, 52.0, 26.5, 25.3, 25.2, (one signal coincident or not observed). ESI MS m/z 730.3 ([M + Na]⁺, 48), 676.3 ([M – OMe]⁺, 100). ESI HRMS m/z calcd. for C₄₆H₄₉NO₄SiNa ([M + Na]⁺) 730.3323, found 730.3311.

**Compound 4e:** To a solution of 4d (0.566 g, 0.799 mmol) in THF (80 mL) at −78 °C was added TBAF (1.0 M in THF, 0.82 mL, 0.82 mmol). The solution was stirred for 1 h at −78 °C before warming the solution to −15 °C and stirring for an additional 30 min. The reaction mixture was then poured into satd. aq. NH₄Cl (150 mL). H₂O (100 mL) was added and the mixture was extracted with CH₂Cl₂ (150 mL, 100 mL). The organic phase was washed with 5% aq. NH₄Cl (150 mL), dried (MgSO₄), filtered, and the solvent removed in vacuo. Column chromatography (silica gel, 4:1 hexanes/EtOAc) afforded 4e (0.354 g, 87%) as an off white foamy solid. Rₜ = 0.31 (4:1 hexanes/EtOAc), 0.50 (CH₂Cl₂). IR (CH₂Cl₂ cast film): 3290 (m), 2056 (w), 2936 (w), 2230 (vw), 2117 (vw), 1594 (s), 1519 (s) cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ 8.64 (s, 2H), 8.50 (s, 2H), 8.09 (d, J = 9.0 Hz, 2H), 8.03–7.96 (m, 4H), 7.60–7.54 (m, 4H), 7.51 (d, J = 9.0 Hz, 2H), 3.12 (s, 1H), 3.11 (s, 3H), 3.08 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 147.1, 133.4, 133.1,
133.0, 132.7, 132.4, 129.5, 128.3, 128.1, 127.3, 127.1, 127.0, 123.4, 96.2, 84.6, 82.4, 78.0, 75.1, 73.9, 52.1, 52.0. ESI MS $m/z$ 532.2 ([M + Na]$^+$, 100). HRMS ESI $m/z$ calcd. for C$_{34}$H$_{23}$NO$_4$Na ([M + Na]$^+$) 532.1519, found 532.1510.

**Compound 5**: To a solution of 4e (0.307 g, 0.602 mmol) and 3a (0.352 g, 0.909 mmol) in THF (7 mL) and diisopropylamine (5.0 mL, 3.6 g, 36 mmol) which had been deoxygenated for 10 min with argon was added Pd(PPh$_3$)$_4$ (0.030 g, 0.026 mmol) and CuCl (0.005 g, 0.05 mmol) followed by additional deoxygenation with argon for 5 min. The solution was stirred for 14 h at rt before being poured into satd. aq. NH$_4$Cl (150 mL). H$_2$O (100 mL) was added and the mixture was extracted with CH$_2$Cl$_2$ (80 mL, 50 mL). The organic phase was washed with 5% aq. NH$_4$Cl (150 mL), dried (MgSO$_4$), filtered, and the solvent removed in vacuo. The crude yellow oil containing 5 was used for the synthesis of 6a without further purification. HRMS ESI $m/z$ calcd. for C$_{52}$H$_{54}$N$_2$O$_4$Si ([M + H]$^+$) 769.4000, found 769.3984.

**Compound 6a**: To a solution of crude 5 (0.602 mmol, based on 4e) in dry THF (20 mL) that had been deoxygenated by bubbling through N$_2$ for 5 min was added SnCl$_2$·2H$_2$O (0.271 g, 1.20 mmol). The solution was stirred at rt for 3 h, poured onto a pad of silica gel, eluted with CH$_2$Cl$_2$, and the solvent was removed in vacuo. Column chromatography (silica gel, CH$_2$Cl$_2$) afforded a blue-green solid. The solid was dissolved in minimum CH$_2$Cl$_2$ (ca. 6 mL) after which was added hexanes (ca. 50 mL). The suspension was cooled to –78 °C and filtered. The solid was washed with hexanes (5 × 5 mL) to afford 6a (0.263 g, 62%) as a blue solid. $R_f$ = 0.99 (CH$_2$Cl$_2$). UV-vis (CH$_2$Cl$_2$) $\lambda_{max}$ (e): 274 (sh, 38 000), 317 (21 6000), 343 (sh, 30 500), 391 (14 300), 440 (7 600), 497 (8 400), 589 (sh, 9 560), 689 (28 400) nm. No significant emission in CH$_2$Cl$_2$. IR (CHCl$_3$, cast) 3045 (w), 2954 (m), 2928 (m), 2857 (w), 2169 (s), 1604 (s), 1590 (s) cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.89 (s, 2H), 8.60 (s, 2H), 8.20 (d, $J$ = 8.5 Hz, 2H), 7.79–7.71 (br s, 4H), 7.70–
7.62 (m, 4H), 7.33–7.26 (m, 4H), 6.73 (d, J = 8.7 Hz, 2H), 3.39 (t, J = 7.7 Hz, 4H), 1.69 (quintet, J = 7.2 Hz, 4H), 1.46–1.34 (m, 12H), 0.95 (t, J = 6.9 Hz, 6H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 148.5, 146.6, 133.3, 132.1, 131.8, 131.6, 130.7, 130.1, 129.2, 128.6, 128.4, 126.5, 125.9, 125.5, 125.1, 123.7, 121.3, 113.9, 111.4, 108.9, 108.3, 101.8, 94.0, 86.8, 51.1, 31.8, 27.3, 26.9, 22.7, 14.1. ESI HRMS \(m/z\) calcd. for C\(_{50}\)H\(_{46}\)N\(_2\)O\(_2\) (M\(^{+}\)) 706.3554, found 706.3542. TGA: \(T_d \approx 285^\circ\)C. DSC: decomposition, 152 °C (onset), 177 °C (peak).

**Compound 8d:** To a solution of 1d (0.076 g, 0.13 mmol) in CH\(_2\)Cl\(_2\) (5 mL) was added tetracyanoethylene (0.012 g, 0.094 mmol). The reaction flask was stirred at rt for 24 h. The solvent was removed \textit{in vacuo} and the residue was purified by column chromatography (silica gel, CH\(_2\)Cl\(_2\)) to afford 8d (0.050 g, 74%) as a yellow solid. \(R_f = 0.70\) (CH\(_2\)Cl\(_2\)). IR (CHCl\(_3\) cast film): 3049 (w), 2941 (s), 2892 (m), 2864 (s), 2250 (vw), 2199 (m), 2149 (w), 1604 (s) cm\(^{-1}\). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 8.993 (s, 1H), 8.987 (s, 1H), 8.12–8.07 (m, 1H), 8.06–8.00 (m, 1H), 7.77–7.72 (m, 2H), 7.72–7.66 (m, 1H), 7.62–7.54 (m, 3H), 7.54–7.48 (m, 2H), 7.06–7.01 (m, 2H), 5.84 (s, 1H), 5.80 (s, 1H), 3.91 (s, 3H), 1.42–1.24 (m, 21H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 160.8, 133.8, 133.70, 133.67, 132.9, 132.9, 131.9, 130.5, 130.4, 130.3, 129.6, 129.5, 128.5, 127.19, 127.16, 127.14, 127.03, 126.99, 120.9, 119.9, 114.5, 114.1, 110.9, 110.8, 110.4, 110.2, 106.0, 102.9, 100.5, 82.1, 55.5, 51.9, 51.7, 45.8, 45.7, 18.9, 11.4 (two signals coincident or not observed). MALDI MS \(m/z\) 716.3 (M\(^{+}\), 5), 588.2 ([M – (NC)\(_2\)C=C(CN)\(_2\)]\(^{+}\), 100). MALDI HRMS \(m/z\) calcd. for C\(_{48}\)H\(_{40}\)N\(_4\)OSi (M\(^{+}\)) 716.2966, found 716.2969.

**Compound 14b:** To a solution of 4b (0.125 g, 0.188 mmol) in CH\(_2\)Cl\(_2\) (9 mL) was added tetracyanoethylene (0.025 g, 0.20 mmol). The reaction flask was stirred at rt for 15 h, poured onto a pad of silica gel, eluted with 3:1 hexanes/EtOAc to collect the red band, and the solvent was removed \textit{in vacuo}. Column chromatography (silica gel, 4:1 hexanes/EtOAc) afforded 14b
(0.104 g, 70%) as a red solid. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.64 (s, 1H), 8.61 (s, 1H), 8.23 (br s, 1H), 7.98 (br s, 1H), 7.86 (d, $J = 8.1$ Hz, 1H), 7.81 (d, $J = 8.1$ Hz, 2H), 7.71 (br s, 1H), 7.58–7.40 (m, 4H), 7.04 (br s, 2H), 5.95 (d, $J = 9.0$ Hz, 2H), 3.52 (s, 3H), 3.00 (s, 3H), 2.67 (s, 6H), 1.26–1.19 (m, 21H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 173.8, 162.4, 152.2, 133.8, 133.5, 133.1, 132.9, 132.6, 132.0, 130.6, 130.4, 130.3, 130.0, 128.5, 128.2, 128.1, 128.0, 127.8, 127.7, 127.2, 127.1, 126.8, 118.6, 113.9, 113.0, 112.3, 110.5, 104.6, 93.4, 82.4, 75.4, 52.3, 51.5, 39.5, 18.7, 11.4 (five signals coincident or not observed). ESI MS $m/z$ 814.4 ([M + Na]$^+$, 100), 760.3 ([M – OMe]$^+$, 40). ESI HRMS $m/z$ calcd. for C$_{51}$H$_{51}$N$_5$O$_2$SiNa ([M + Na]$^+$) 814.3548, found 814.3537.

**Supplementary data**

Supplementary data are available with the article through the journal Web site at


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See the Supporting Information for UV–vis absorption spectra of the pentacenes presented herein.

See the Supporting Information for details.

The wavelength used as the absorption edge for determining $E_g^{opt}$ corresponds to the lowest energy absorption wavelength that has a molar absorptivity (☐) ≥ 1000 L·mol$^{-1}$·cm$^{-1}$.

Potential values ($E$) were calculated using the following equation (except where otherwise noted): $E = (E_{pc} + E_{pa})/2$, where $E_{pc}$ and $E_{pa}$ correspond to the cathodic and anodic peak potentials, respectively. All potentials represent a one-electron reduction or oxidation event. $E_g^{electro}$ determined from the separation between the first oxidation and first reduction potentials.

Interplanar distances were calculated from the distance between the least squares planes generated from the carbon atoms of the pentacenes moieties.


