SUPPORTING INFORMATION

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General Experimental

All manipulations were performed under an inert-gas atmosphere of dried argon in standard (Schlenk) glassware which was flame dried with a Bunsen burner prior to use. Solvents were dried according to standard procedures and saturated with Ar. The deuterated solvents used for the NMR spectroscopic measurements were degassed by three successive "freeze-pump-thaw" cycles and dried over Calciumhydride or Sodium. Solids were separated by suspensions by filtration with the aid of a filter canula or if necessary by centrifugation thus avoiding filtration procedures. The 1H and 13C NMR spectra were recorded on a Bruker AVANCE 200, 400 and 600 spectrometers equipped with variable temperature units. Infrared spectroscopy was carried out on a Varian 3100 FT-IR-Spectrometer from Biorad. Elemental analyses were carried out in the microanalytical laboratory of the chemistry department at Heidelberg. 4,9-Diaminoperylene-quinone-3,10-diimine (DPDI) was synthesized as reported previously.1 All other starting materials were obtained commercially and used without further purification.

1. Preparation of the Compounds

Preparation of 1: To a solution of 365 mg (1.2 mmol) 3,4,9,10-tetraaminoperylene in 40 ml THF were added 1.9 ml (4.8 mmol) n-butyllithium (2.5 M in hexane) at -60 °C. The deep blue solution was allowed to warm to room temperature and stirred for one hour. The solution was cooled to -60 °C and treated with 521 mg (4.8 mmol) trimethylsilylechloride. The solution was allowed to warm to room temperature and stirred over night. The solvent was removed in vacuo and the remaining red residue was extracted twice with 30 ml toluene each. The solvent of the filtrate was removed in vacuo yielding 261 mg (0.4 mmol, 75%) of a deep red solid.

Preparation of 2: To a solution of 300 mg (0.5 mmol) of compound 1 in 30 ml THF was slowly added 1.0 ml (1.0 mmol) borane-thf adduct (1 M in THF) at -60 °C. The solution was allowed to warm to room temperature and stirred over night. The reaction mixture was evaporated to dryness. The remaining residue was extracted twice with 30 ml toluene each. The solvent of the filtrate was removed in vacuo yielding 261 mg (0.4 mmol, 75%) of a deep red solid.

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Preparation of 3: To a solution of 300 mg (0.5 mmol) of compound 1 in 30 ml toluene were added 2.0 ml (1.0 mmol) alane-N,N-dimethylethylamine adduct (0.5 M in toluene) at -60 °C. The solution was allowed to warm to room temperature and stirred over night. The reaction mixture was evaporated to dryness. The remaining residue was washed with 3 x 10 ml cold hexane and dried in vacuo yielding 261 mg (0.4 mmol, 75%) of a violet solid.

Preparation of 4: To a solution of 300 mg (0.5 mmol) of compound 1 in 30 ml THF were added 1.6 ml (2.0 mmol) borane-thf adduct (1 M in THF) at -60 °C. The solution was allowed to warm to room temperature and stirred over night. The reaction mixture was evaporated to dryness. The remaining residue was extracted twice with 30 ml toluene each. The solvent of the filtrate was removed in vacuo yielding 261 mg (0.4 mmol, 75%) of a deep red solid.

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butyllithium (2.5 M in hexane) at -60 °C. The deep blue solution was allowed to warm to room temperature and stirred for two hours. The solvent was removed in vacuo and the remaining solid was dissolved in toluene, cooled to -60 °C and treated with 1 ml (1 mmol) dichloromethylaluminium. The reaction mixture was warmed to room temperature and stirred overnight. With the aid of a filter canula the solids were separated and the filtrate was evaporated to dryness, washed twice with hexane and dried in vacuo yielding 256 mg (0.3 mmol, 62%) of a deep red solid. ¹H-NMR (600.13 MHz, CDCl₃, 295 K) δ = 7.74 (d, J = 8.3 Hz, 4 H, H¹), 6.69 (d, J = 8.3 Hz, 4 H, H²), 3.85 (m, 8 H, thf), 1.73 (m, 8 H, thf), 0.25 (s, 36 H, Si(CH₃)₃), -0.53 (s, 6 H, AlCH₃). ¹⁳C-NMR (150.92 MHz, CDCl₃, 295 K) δ = 148.7 (C6), 132.1 (C2), 126.4 (C1), 124.5 (C3), 119.0 (C5), 118.8 (C4), 68.5 (thf), 25.0 (thf), 3.0 (Si(CH₃)₃), n.o. (AlCH₃). ²⁹Si-NMR (79 MHz, C₂D₆, 295 K) δ = -1.25. IR (KBr, cm⁻¹) ν = 2954w, 2898 w, 1562 m, 1399 s, 1261 s, 1063 m, 849 s. Elemental analysis calculated (%) for C₂₉H₆₆Al₄N₄O₄Si₄: C 61.12 H 8.06 N 6.62. Found C 61.10 H 8.25 N 6.62.

2. Crystal structure analyses of 2 and 5:

Suitable single crystals of compound 2 were obtained by slow cooling of a solution in diethyl ether to -30 °C. Suitable single crystals of compound 5 were obtained by slow cooling of a solution in toluene. Intensity data were collected at low temperature with a Bruker AXS Smart 1000 CCD diffractometer (Mo-Kα radiation, graphite monochromator, λ = 0.71073 Å). Data were corrected for for air and detector absorption, Lorentz and polarization effects; absorption by the crystal was treated with a semiempirical multiscan method. The structures were solved by conventional direct methods and refined by full-matrix least squares methods based on F² against all unique reflections. All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were either taken from difference Fourier syntheses and refined (compound 2), or input at calculated positions and refined with a riding model (compound 5).

3. Photophysical Measurements:

The UV-Vis absorption spectra were recorded on a Cary 5000 UV-Vis-NIR spectrophotometer and were baseline and solvent corrected (Figure S1). Emission spectra were recorded on a Varian Cary Eclipse Spectrometer and standard corrections were applied to all spectra (Figure S2).

All measurements were carried out under strictly anaerobic conditions and at ambient temperature.

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²SÁINT, Bruker AXS, 2007
⁵G. M. Sheldrick, SHELX-97, University of Göttingen, 1997.
Calculating the Fluorescence Lifetimes according to the Strickler-Berg equation: (Strickler, S. J.; Berg, R. A. J. Chem. Phys. 1962, 37, 814-822.)

\[ \frac{1}{\tau_0} = 2.850 \times 10^5 \eta^2 \int \frac{I(t) \, dt}{\omega^{3/2}(\omega + \omega_0)} \int \frac{\epsilon(t) \, dt}{\omega} \]

Absorbance and emission spectra were recorded in diluted \((10^{-5}\text{ mol/l})\) solutions. \(\eta\) is the refractive index of the solvent.

To obtain \(A\) two curves were plotted, one of the corrected fluorescence intensity against the frequency in wavenumbers, and the other \(\nu^{-3}\) this value. The ratio of the areas under the curves then gives \(A\).