Supporting Information

Efficient Deep-Red Light-Emitting Electrochemical Cells based on a Perylenediimide-Iridium-Complex Dyad

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Instrumentation and Materials

All reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. Commercial TLC plates (silica gel 60 F254, SDS) were used to monitor the progress of the reaction, with spots observed under UV light at 254 and 365 nm. Column chromatography was performed with silica gel 60A (particle size 40-63 μm, SDS). NMR spectra were taken using a 300 MHz Bruker AC-300. Ultraviolet–visible (UV-vis) absorption measurements were taken on a ThermoSpectronic Helios γ spectrophotometer. Infrared measurements were taken with a Fourier Transform (FT-IR) ThermoNicolet model IR 200 Spectrometer in transmission method with KBr. Mass spectra were obtained from a Bruker Reflex III matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) spectrometer using dithranol as a matrix. Elemental analyses were performed on a LECO CHNS-932 elemental analyzator.

Room-temperature photoluminescence emission (PL) spectra were measured using a Varian-Carry Eclipse spectrofluorimeter, equipped with a photodiode to correct the PL spectra and a photomultiplier tube. The characteristics of the latter were accounted for in the PL spectra. The PL quantum yield measurements in degassed acetonitrile solvent of $[Ir(ppy)_2phen][PF_6]$ and **1** were performed with the Hamamatsu model C9920-01, which consists of a xenon lamp, an integration sphere and a multi-channel analyzer at 360 and 550 nm excitation wavelengths. The quantum yield of **1** was determined in a deaerated acetonitrile solution at an excitation wavelength of 550 nm using molecule **2** as the reference substance. The excited-state lifetime was measured from fresh solutions, which were degassed by N_2 bubbling for 30 min. A laser flash-photolysis system based on a pulsed Nd:YAG laser (using 550 nm as exciting wavelength) was used. The single pulses were approximately 10 ns duration and the energy was approximately 10 mJ/pulse. A Lo255 Oriel xenon lamp was employed as light source. The laser flash-photolysis apparatus consisted of the pulsed laser, the Xe lamp, a 77200 Oriel monochromator and an Oriel photomultiplier (PMT) system made up of 77348 PMT power supply. The oscilloscope was a TDS-640A Tektronix.

Computational Details. Density functional calculations (DFT) were carried out with the C.02 revision of the Gaussian 03 program package,[1] using Becke's three-parameter B3LYP exchange–correlation functional[2,3] together with the 6-31G** basis set for C, H, and N atoms[4] and the ''double-ζ'' quality LANL2DZ basis set for the Ir element.[5] An effective core potential (ECP) replaces the inner core electrons of Ir leaving the outer core $(5s)^2(5p)^6$ electrons and the $(5d)^6$ valence electrons of Ir(III). The geometries of the singlet ground state (S_0) were fully optimized without imposing any symmetry restriction. Solvent effects were considered within the SCRF (self-consistent reaction field) theory using the polarized continuum model (PCM) approach to model the interaction with the solvent.[6,7] Molecular orbitals were calculated in acetonitrile solution using gas-phase optimized geometries. The structure of the molecule was simplified by substituting alkyl chains by methyl groups in order to reduce the computer time.

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Device preparation and characterization. PEDOT:PSS was purchased from HC-Starck and solvents used were purchased from Aldrich. Indium-tin oxide (ITO)-coated glass plates (15 Ω □$^{-1}$) were patterned using conventional photolithography (obtained from Naranjosubstrates, www.naranjosubstrates.com). The substrates were cleaned by sonification subsequently in soap water, water and 2-propanol baths. After drying, the substrates were placed in a UV-ozone cleaner (Jelight 42-220) for 20 minutes.

The electroluminescent devices were prepared as follows: transparent thin films of the active layer containing compound **1** together with the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate in molar ratio 2:1 were obtained by spinning from acetonitrile solutions using concentrations of 20 mg/mL at 1000 rpm for 20 seconds, resulting in a 80 nm thick film. Prior to deposition of the emitting layer, a 100 nm layer of PEDOT:PSS was deposited to increase the device preparation yield. The thickness of the films was determined using an Ambios XP1 profilometer. After spinning the organic layers, the samples were transferred to an inert atmosphere glovebox (< 0.1 ppm O_2 and H_2O, MBraun). Aluminum metal electrodes (80 nm) were vapor-deposited using a shadow mask in an Edwards Auto500 evaporator ($p < 1\times10^{-6}$ mbar) within an inert atmosphere glovebox.

Current density and luminance versus voltage were measured using a Keithley 2400 source meter and a photodiode coupled to a Keithley 6485 pico-ampmeter using a Minolta LS100 to calibrate the photocurrent. External quantum efficiencies (EQE) were determined using an integrated sphere coupled to an UDT instruments S370 Optometer. An Avantes luminance spectrometer was used to measure the EL spectrum. Lifetime data were obtained by applying a constant voltage over the device and monitoring the current flow and simultaneously the current generated by a Si-photodiode calibrated using a Minolta LS100 luminance meter.

General Procedure and Compound data

Synthesis of 2

N-(2´-Ethylhexyl)-1,6,7,12-*tetrakis*-[4´(1´´,1´´,3´´,3´´-tetramethylbutyl)phenoxy]perylene-9,10-dicarboximide-3,4-dicarboxyanhydride **2** was prepared as reported in the literature: *J. Mater. Chem.*, 2008, **18**, 5802–5808.

Synthesis of *N´*-(1´´,10´´-phenanthroline-5´´-yl)-*N*-(2´-ethylhexyl)-1,6,7,12-*tetrakis*-[4´(1´´,1´´,3´´,3´´-tetramethylbutyl)phenoxy]-perylene-3,4:9,10- tetracarboxidiimide (3).

N-(2'-Ethylhexyl)-1,6,7,12-tetrakis-[4'(1'',1'',3'',3''-tetramethylbutyl)phenoxy]perylene-9,10-dicarboximide-3,4-dicarboxyanhydride **2** (200 mg, 0.15 mmol) was reacted with 5-amino-1,10-phenanthroline (65 mg, 0.3 mmol) and zinc acetate as catalyst (12 mg) in quinoline (10 mL) for 10 h at 180 ºC. After being cooled to room temperature, the mixture was poured onto aqueous HCl (200 mL, 2N). The resulting precipitate was isolated by filtration. The crude product was dissolved in CH_2Cl_2, transferred to a separating funnel, washed 3 times with a saturated $NaHCO_3$ solution and finally washed with water. The combined CH_2Cl_2 extracts were dried over anhydrous $MgSO_4$, filtered and concentrated. Purification was achieved by repetitive column chromatography on silica-gel using CH_2Cl_2/MeOH 9.5:0.5 as eluent to give **3** as dark-purple solid (158 mg, 70%).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 ºC): δ= 9.24 (dd, 1H, *J* = 4.4, 1.7 Hz, Phenanthroline-H_2), 9.19 (dd, 1H, *J* = 4.4,1.7 Hz, Phenanthroline-H_9), 8.23 (dd, 1H, *J*= 8.1, 1.7 Hz, Phenanthroline-H_4), 8.19 (s, 4H, $Ar_{perylene}$), 7.99 (dd, 1H, *J* = 8.1, 1.7 Hz, Phenanthroline-H_7), 7.79 (s, 1H, Phenanthroline-H_6), 7.66 (dd, 1H, *J* = 8.1, 4.4 Hz, Phenanthroline-H_3), 7.55 (dd, 1H, *J* = 8.1, 4.4 Hz, Phenanthroline-H_8), 7.29 (d, 4H, *J*= 8.6 Hz, Ar_{phenol}), 7.25 (d, 4H, *J*= 8.6 Hz, Ar_{phenol}), 6.89 (d, 4H, *J*= 8.6, Ar_{phenol}), 6.86 (d, 4H, *J*= 8.6, Ar_{phenol}), 4.05 (m, 2H, N-$\underline{CH_2}$-), 1.87 (m, 1H, -CH_2-$\underline{CH}$-), 1.74 (s, 4H, *t*-octyl), 1.68 (s, 4H, *t*-octyl), 1.38 (s, 12H, *t*-octyl), 1.30 (s, 12H, *t*-octyl), 1.34-1.23 (m, 8H, -CH_2-) , 0.89 (t, 3H, *J* = 7,1 Hz, -CH_3), 0.86 (t, 3H, *J* = 7,1 Hz, -CH_3), 0.79 (s, 18H, *t*-octyl), 0.71 (s, 18H, *t*-octyl). ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ= 163.70, 163.57, 156.60, 156.58, 156.23, 152.43, 152.36, 152.31, 146.97, 146.91, 133.12, 132.83, 130.87, 127.87, 127.76,

127.40, 127.24, 126.07, 124.50, 123.37, 122.89, 121.81, 120.97, 119.83, 119.785, 119.66, 119.36, 119.20, 115.07, 57.08, 57.01, 38.39, 38.31, 32.45, 32.37, 31.88, 31.79, 31.47, 30.75, 29.67, 28.70, 24.04, 23.04, 14.09, 10.64. UV (CH_2Cl_2): λ_{max} [$\varepsilon(M^{-1}cm^{-1})$] = 234 (1.07 x 10^5), 265 (7.2 x 10^4), 452 (1.61 x 10^4), 546 (2.67 x 10^4), 586 (4.45 x 10^4) nm. MS: MALDI-TOF (dithranol): m/z: 1497 [M^+], 1498 [$M^+ + 1$]. ν_{max}(KBr)/cm^{-1} 2955, 1703 (C=O imide), 1665 (C=O imide), 1589, 1503, 1409, 1340, 1312, 1287, 1214, 1173. $C_{100}H_{112}N_4O_8$: Calcd: C, 80.18; H, 7.54; N, 3,74. Found: C, 79.80; H, 7.82; N, 3.50%.

Synthesis of {[*N´*-(1´´,10´´-phenanthroline-5´´-yl)-*N*-(2´-ethylhexyl)-1,6,7,12-*tetrakis*-[4´(1´´,1´´,3´´,3´´-tetramethylbutyl)phenoxy]-perylene-3,4:9,10-tetracarboxidiimide]-*bis*-(2-phenylpyridine)-iridium (III)} hexafluorophosphate (1).

Perylene **3** (77 mg, 0.05 mmol) was reacted with *tetrakis*-(2-phenylpyridine)-*bis*-(μ-chloro)-diiridium(III) (27 mg, 0.025 mmol) in ethylene glycol (3 mL) for 15 h at reflux under argon atmosphere. Upon cooling to room temperature, the mixture was transferred to a separating funnel with water and washed 3 times with diethyl ether. The aqueous layer was heated to 60 ºC for 30 minutes to remove residual diethyl ether. 10 mL of aqueous ammonium hexafluorophosphate solution (1 g in 10 mL) were added to the cold reaction mixture producing a precipitate. This solid was filtered, dried, washed and centrifuged 3 times with pentane to give **1** as dark red-purple solid (60 mg, 55%).

^{1}H-NMR (300 MHz, $CDCl_3$, 25 ºC): δ= 8.96 (dd, 1H, *J* = 8.5, 1.3 Hz, Phenanthroline-H_2), 8.92 (dd, 1H, *J* = 8.5, 1.3 Hz, Phenanthroline-H_9), 8.58 (s, 1H, Phenanthroline-H_6), 8.51 (dd, 1H, *J* = 5.1, 1.3 Hz, Phenanthroline-H_4), 8.47 (dd, 1H, *J* = 5.1, 1.3 Hz, Phenanthroline-H_7), 8.24 (t, 2H, *J* = 7.4 Hz, Phenylpyridine$_{pyridyl}$-H_4), 8.14 (s, 2H, $Ar_{perylene}$), 8.14-8.08 (m, 1H, Phenanthroline-H_3), 8.08 (s, 2H, $Ar_{perylene}$), 8.01-7.86 (m, 5H, Phenanthroline-H_8, Phenylpyridine$_{phenyl}$-H_3, Phenylpyridine$_{pyridyl}$-H_5), 7.56 (d, 2H, *J* = 5.2 Hz, Phenylpyridine$_{pyridyl}$-H_6), 7.47-7.38 (m, 8H, Ar_{phenol}), 7.12-6.94 (m, 14H, Ar_{phenol}, Phenylpyridine$_{phenyl}$-H_4, Phenylpyridine$_{phenyl}$-H_5, Phenylpyridine$_{pyridyl}$-H_3), 6.45 (dd, 2H, *J* = 7.5, 3.5 Hz, Phenylpyridine$_{phenyl}$-H_6), 4.01 (m, 2H, N-

$\underline{CH_2}$-), 1.90 (m, 1H, -CH_2-$\underline{CH}$-), 1.81 (s, 4H, *t*-octyl), 1.78 (s, 2H, *t*-octyl), 1.75 (s, 2H, *t*-octyl), 1.41-1.21 (m, 32H, *t*-octyl and -CH_2-), 0.88 (t, 3H, J = 7,3 Hz, -CH_3), 0.87 (t, 3H, J = 7,3 Hz, -CH_3), 0.81 (s, 18H, *t*-octyl), 0.75 (s, 9H, *t*-octyl), 0.72 (s, 9H, *t*-octyl). ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ= 167.59, 163.13, 162.87, 156.50, 156.33, 155.89, 155.85, 152.68, 152.57, 152.52, 151.63, 149.40, 149.35, 146.70, 146.66, 144.13, 138.53, 138.38, 135.14, 133.47, 132.95, 131.62, 130.49, 130.25, 127.88, 127.81, 127.75, 127.39, 127.33, 127.25, 125.03, 124.82, 124.66, 123.40, 123.18, 122.65, 122.53, 120.42, 119.99, 119.60, 119.52, 119.42, 118.82, 118.58, 118.55, 56.56, 56.44, 38.04, 38.00, 31.99, 31.93, 31.90, 31.27, 31.23, 31.18, 31.00, 23.68, 22.62, 13.33, 9.91. UV (CH_2Cl_2): λ_{max} [$\varepsilon(M^{-1}cm^{-1})$] = 235 (1.12 x 10^5), 252 (9.92 x 10^4), 266 (9.78 x 10^4), 379 (1.32 x 10^4), 454 (1.66 x 10^4), 553 (2.78 x 10^4), 593 (4.45 x 10^4) nm. HR-MALDI-TOF MS: *m/z* = 1995.9298. Calcd for $C_{122}H_{128}N_6O_8{}^{191}Ir$.: 1995.9400 $[M]^+$. ν_{max}(KBr)/cm^{-1} 2954, 1703 (C=O imide), 1664 (C=O imide), 1587, 1503, 1479, 1410, 1340, 1313, 1288, 1214, 1173, 843. $C_{122}H_{128}F_6IrN_6O_8P.5H_20$: Calcd: C, 65.60; H, 6.23; N, 3.76. Found: C, 65.17; H, 6.25; N, 3.69%.

* = solvents and water

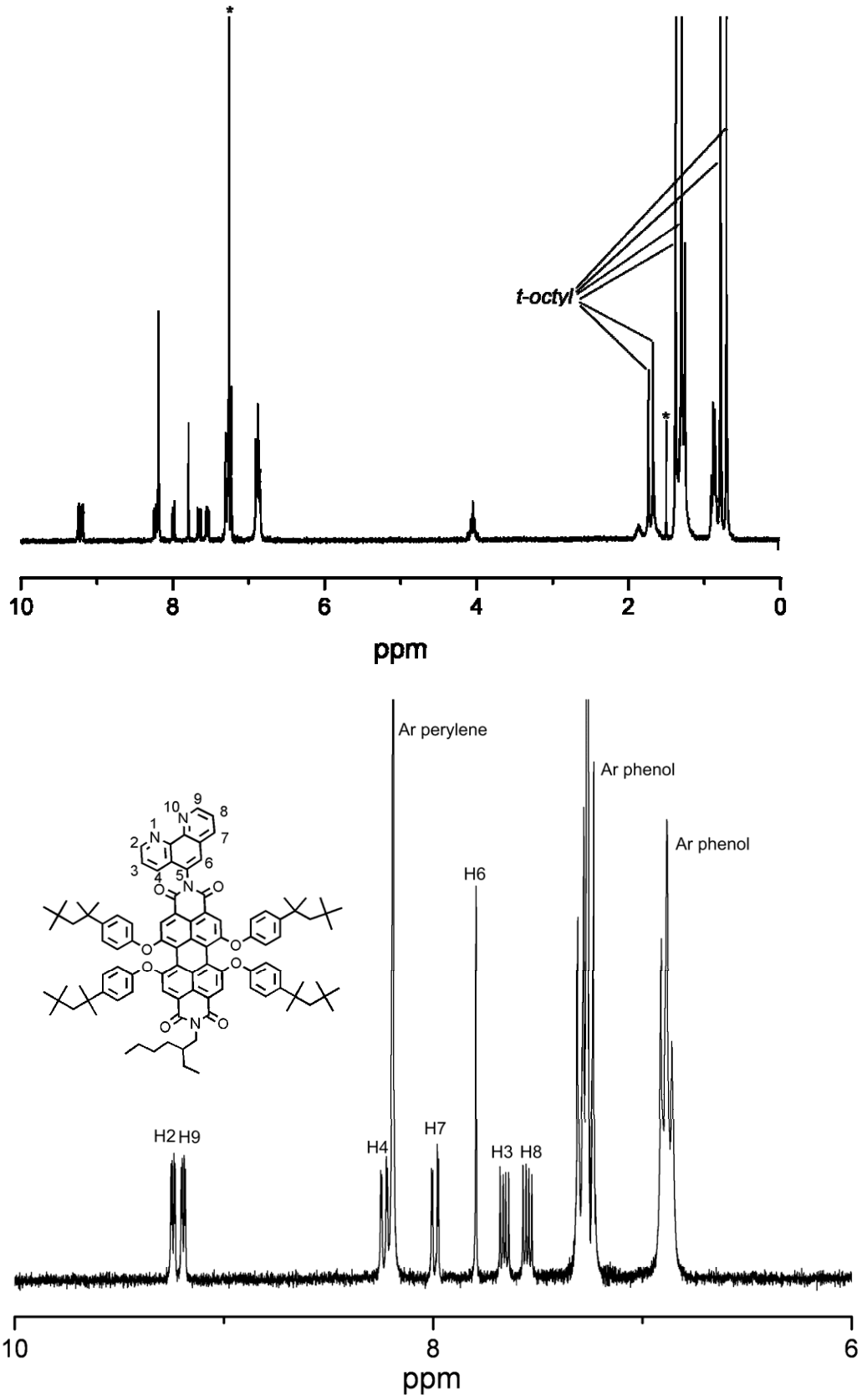

Figure S8. ^{1}H NMR spectrum of **3** in $CDCl_3$.

* = solvent and water

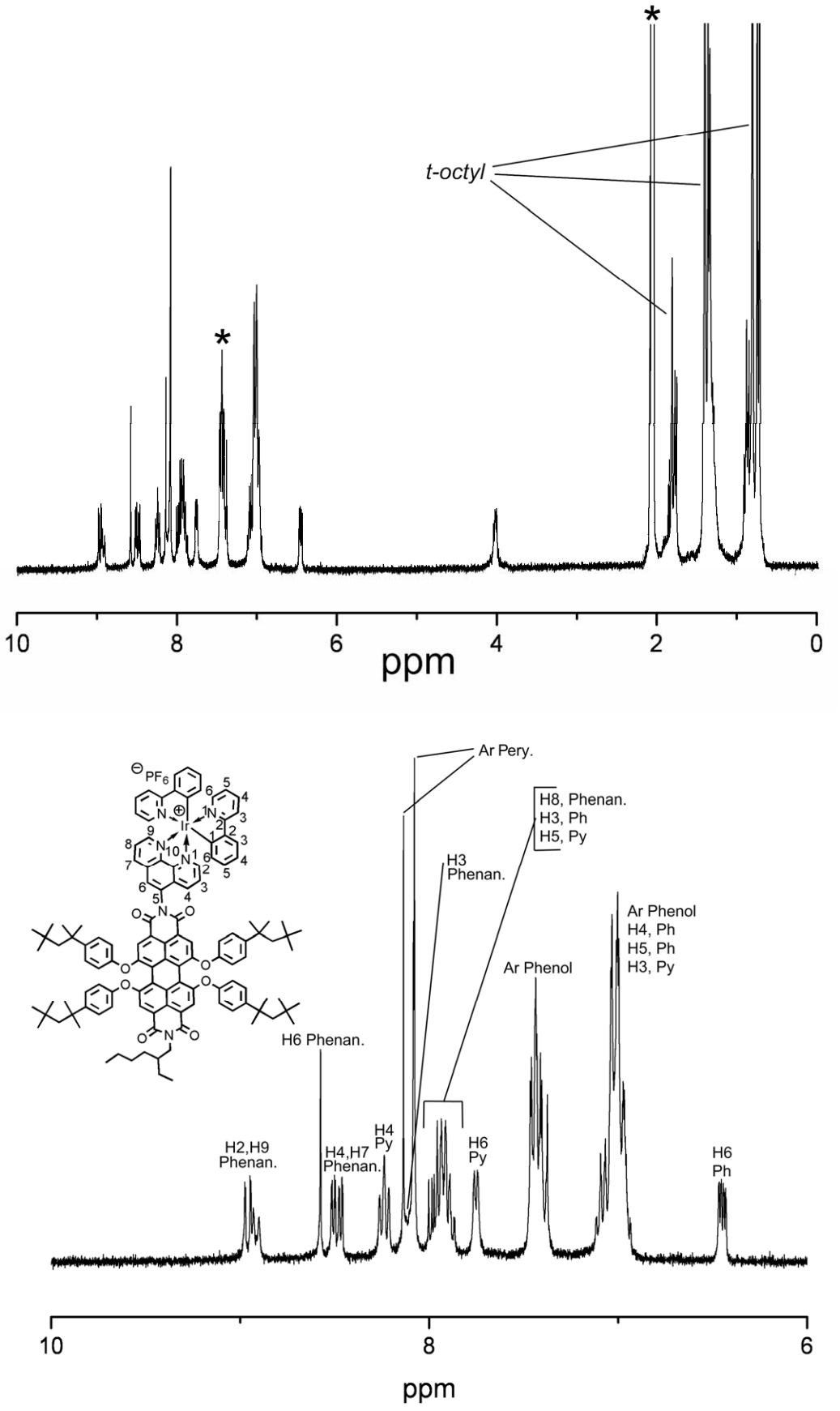

Figure S9. ^{1}H NMR spectrum of **1** in $CDCl_3$.

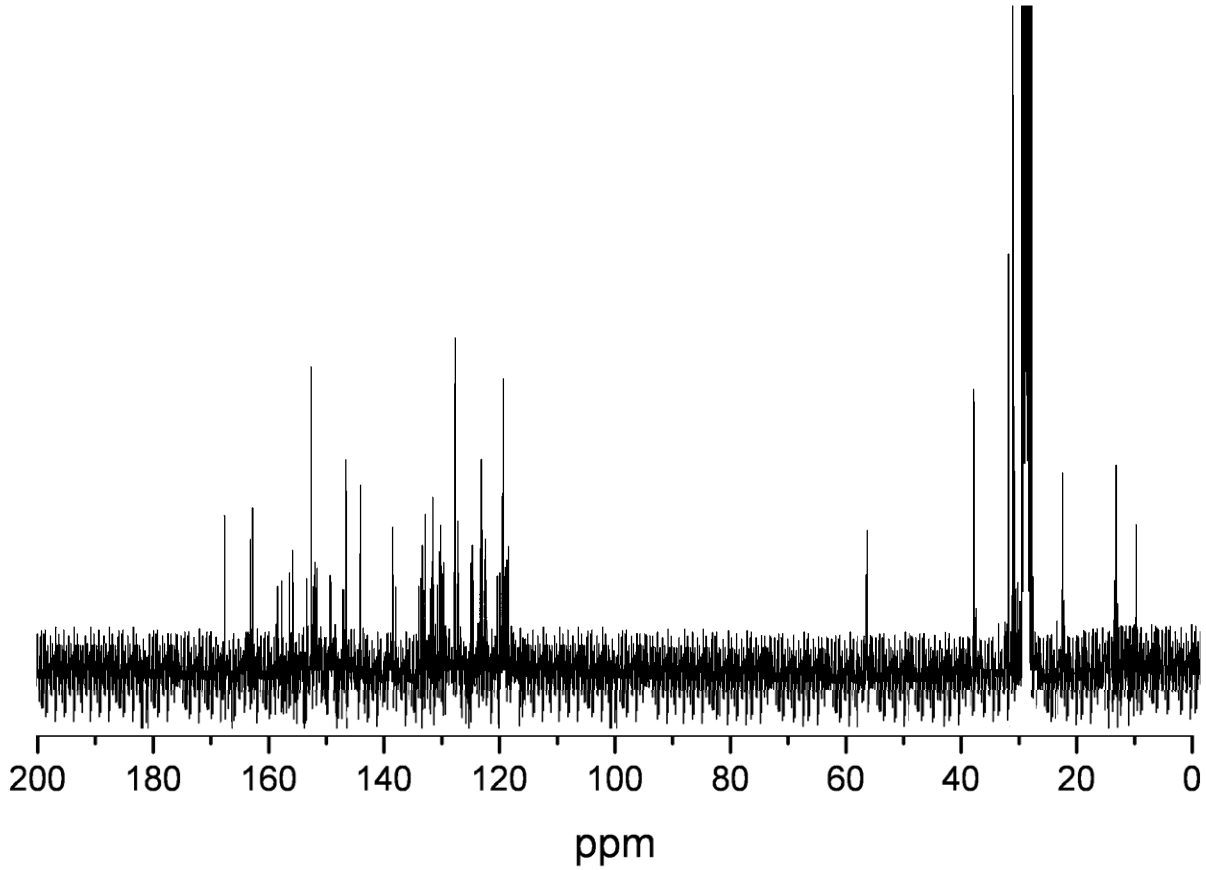

Figure S10. ^{13}C NMR spectrum of **1** in acetone-d_6.

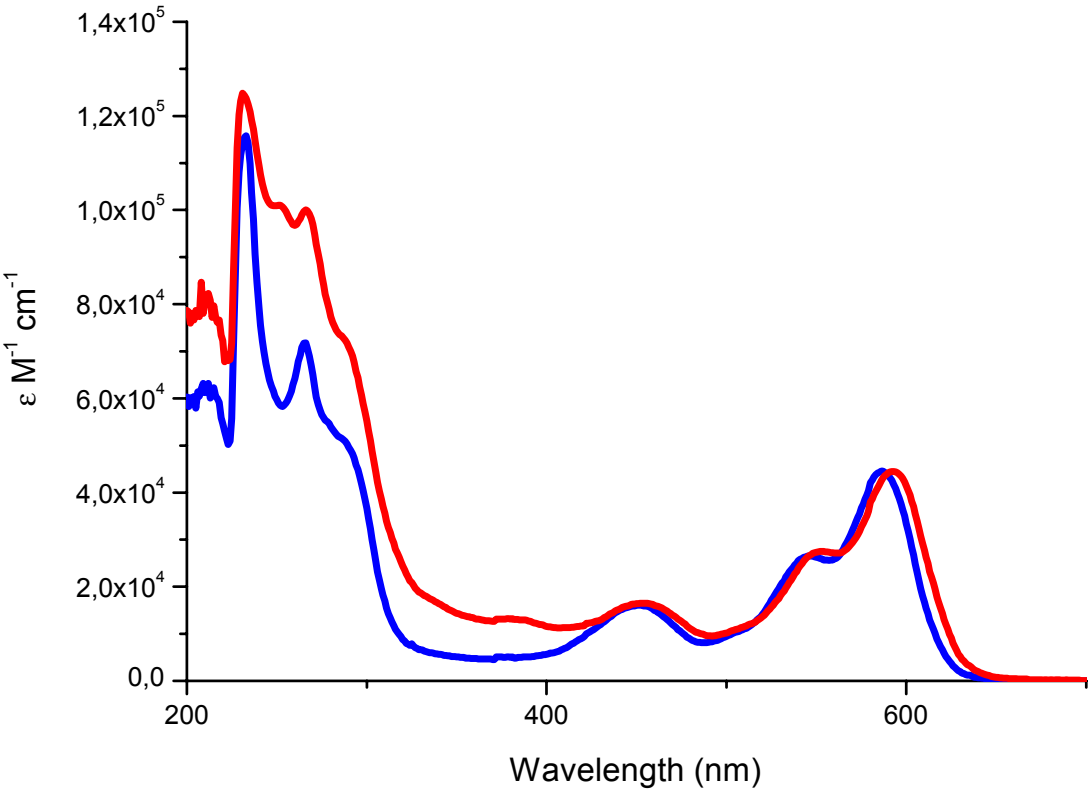

Figure S11. UV-vis absorption spectra of **1** (red) and **3** (blue) in CH_2Cl_2.

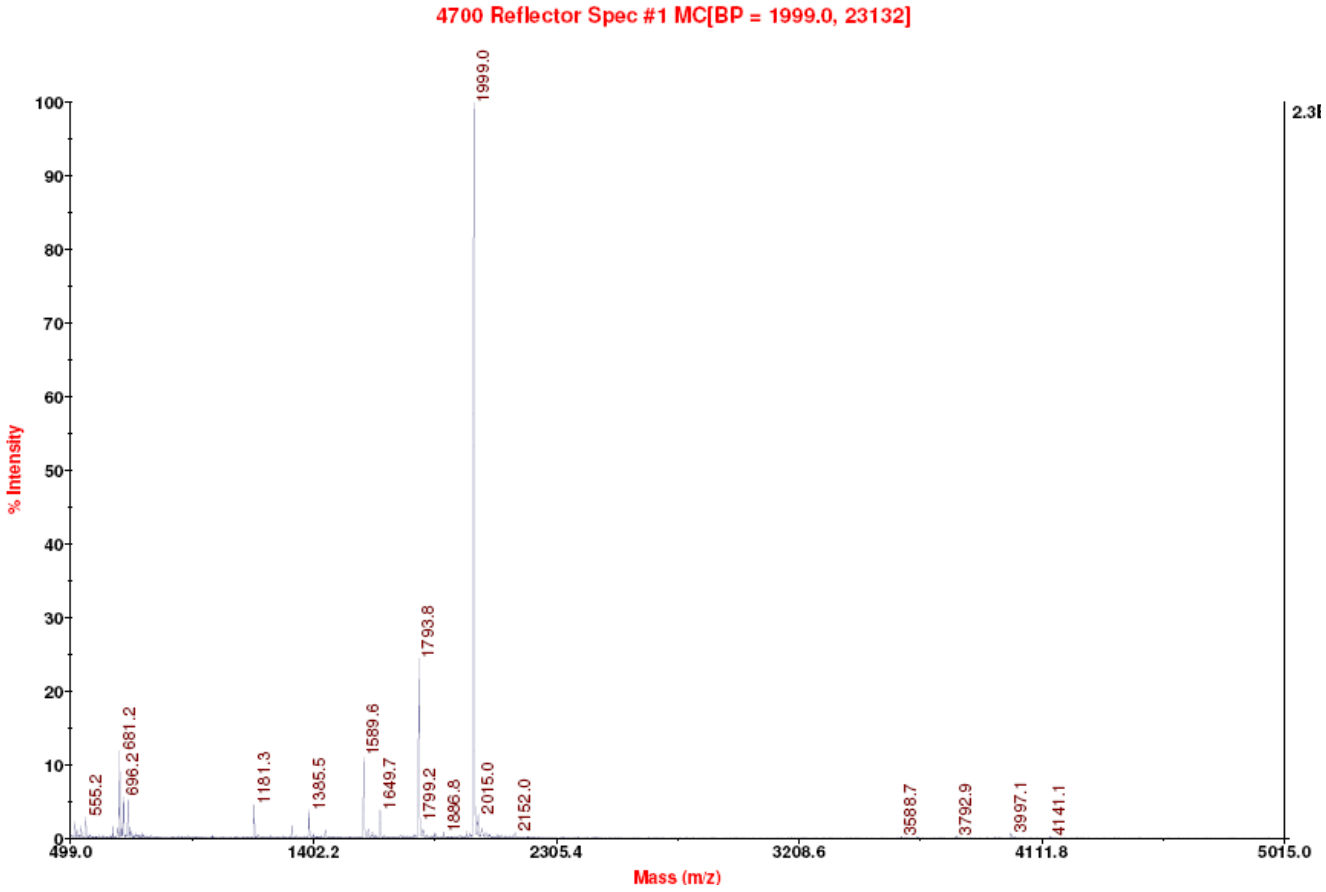

Figure S12a. MALDI mass spectrum of **1** (positive mode).

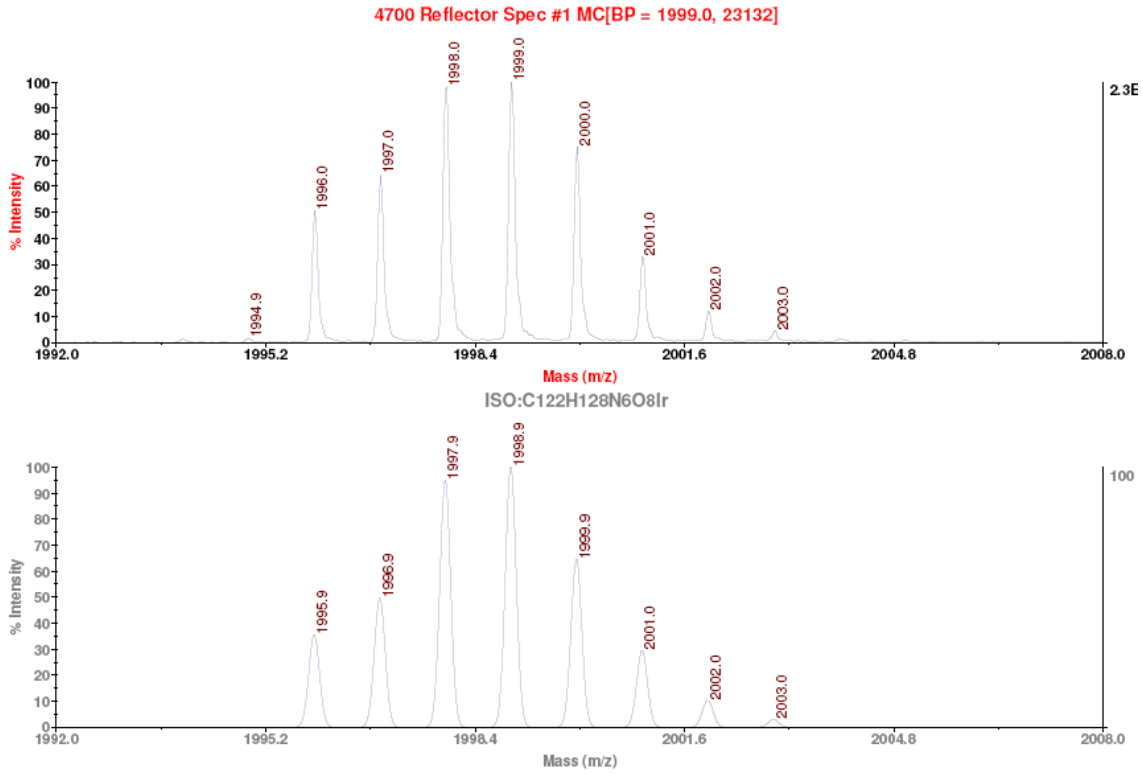

Figure S12b. Isotopic distribution of **1** (mass spectra).

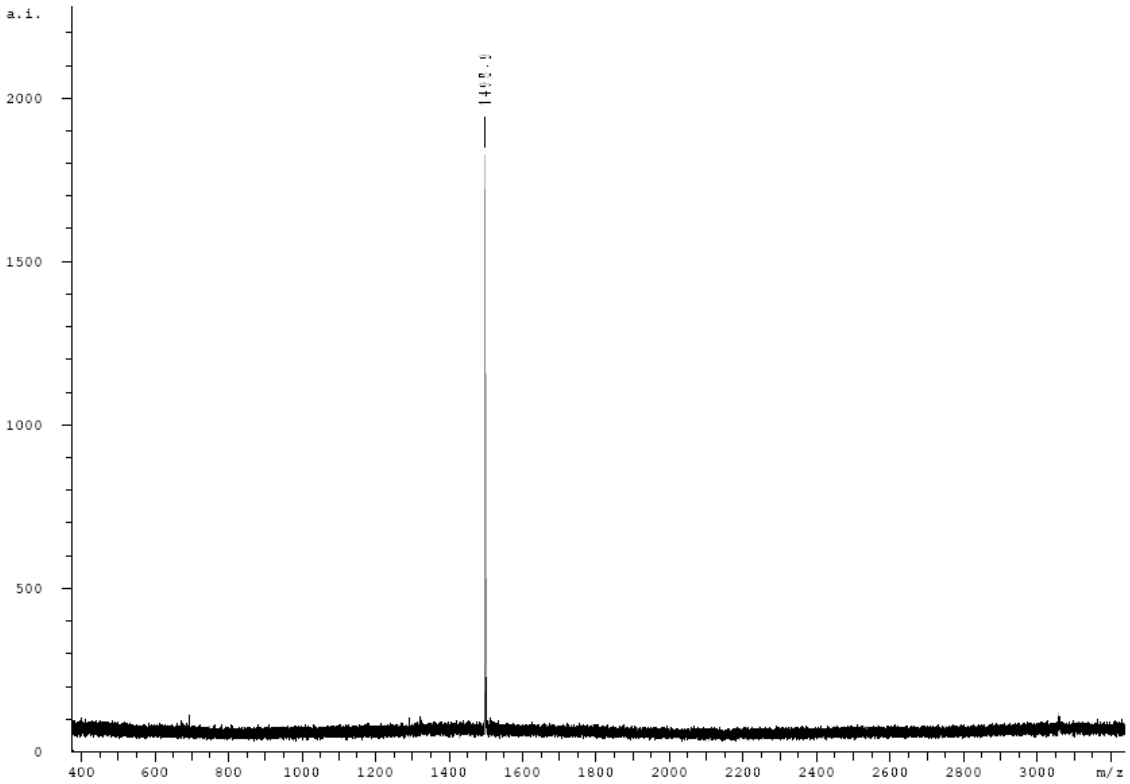

Figure S13a. MALDI mass spectrum of **3** (positive mode).

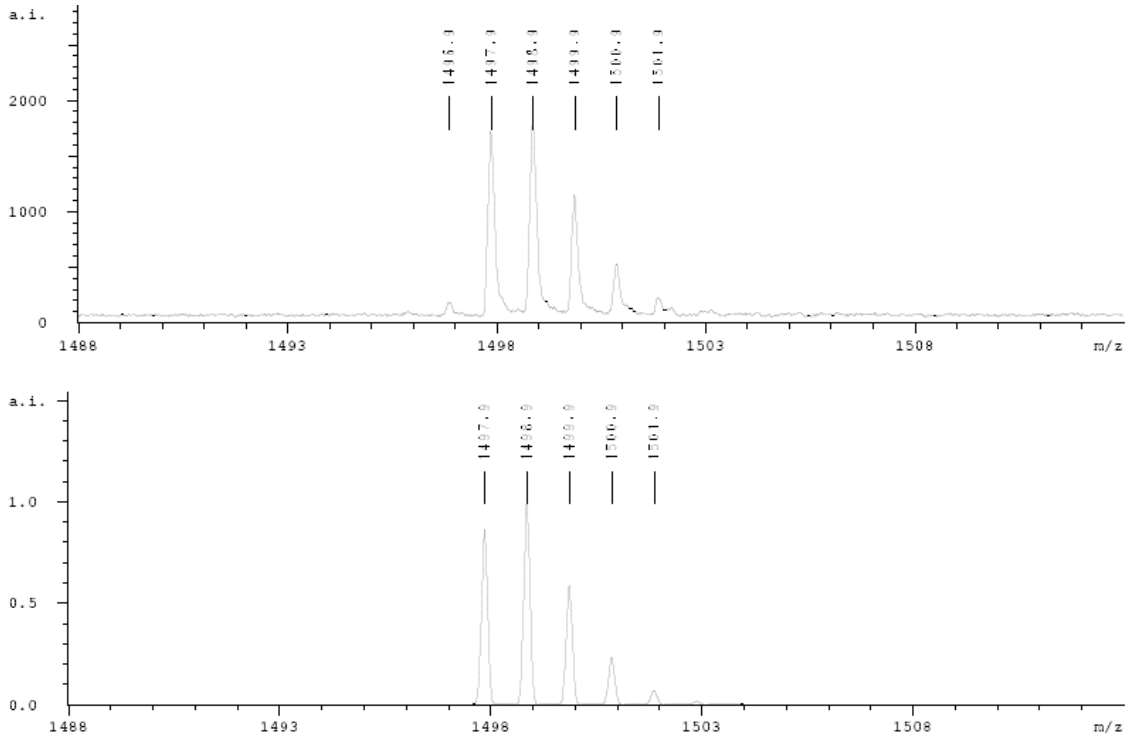

Figure S13b. Isotopic distribution of **3** (mass spectra).