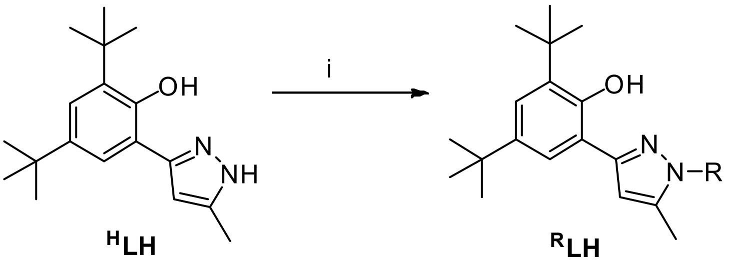
Electronic Supporting Information

Experimental

THF was distilled from Na/benzophenone-ketyl. Dry distilled CH_2Cl_2 and MeCN were purchased from Aldrich Chemical Ltd. Commercially available, solid chemicals were used without further purification, liquids were generally freshly distilled. Organic chemicals were purchased from Fluka, Acros and Aldrich. $Cu(BF_4)_2 \cdot 6H_2O$, was purchased from Acros.



Scheme S1: (i) NaH,RI,THF,0°C 12hr

2,4-di-tert-butyl-6-(1,5-dimethyl-1H-pyrazol-3-yl)phenol (^{Me}LH)

A solution of 500 mg (1.7 mmol) of **^{H}LH** in 10 mL of dry THF was slowly treated with 75 mg (1.7 mmol) of NaH at 0°C. The mixture was warmed up to room temperature and stirred for a further 2 h until hydrogen evolution ceased. 0.1 mL (1.7 mmol) of methyliodide dissolved in 5 mL of dry THF were added dropwise and the resulting mixture was stirred for 12 h at room temperature. The solvent was removed under vacuum and the sticky material was redissolved in CH_2Cl_2 (20 mL) and washed with water (20 mL). The water phase was extracted three times with 20 mL of CH_2Cl_2 and the organic phases were combined, dried over $MgSO_4$, and the solvent was evaporated. The resulting residue was recrystallised from methanol to yield a light-yellow powder of **^{Me}LH** in Yield: 360 mg (68 %). Elemental analysis: Calc. for $C_{18}H_{26}N_2O$: C 75.01, H 9.39, N 9.32; Found: C 75.01, H 9.50, N 9.31. ^1H NMR ($CDCl_3$, 300 MHz): δ 11.2 (s, 1H, OH), 7.38 (d, 2.4 Hz, 1H, Ar), 7.25 (d, 2.4 Hz, 1H, Ar), 6.40 (d, 0.6 Hz, 1H, pz), 2.32 (d, 0.6 Hz, 3H, CH_3), 1.47 (s, 9 H, ^{t}*Bu*), 1.33 (s, 9 H, ^{t}*Bu*). ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ 152.57, 150.94, 140.29, 139.19, 136.27, 123.46, 120.80,116.03, 102.20, 35.95, 35.14, 34.20, 31.64, 29.64, 11.02. M.p. 130 °C. M.S ES(+): m/z 301 (MH^+).

IR (ZnSe): ν 2951, 1568, 1607, 1465, 1377, 1359 cm^{-1}.

2,4-di-tert-butyl-6-(5-methyl-1-propyl-1H-pyrazol-3-yl)phenol (^{Pr}LH)

A solution of 500 mg (1.87 mmol) of **^{H}LH** in 10 mL of dry THF was slowly treated with 75 mg (1.87 mmol) of NaH at 0°C. The mixture was warmed up to room temperature and stirred for a further 2 h until hydrogen evolution ceased. 0.18 mL (1.87 mmol) of propyliodide dissolved in 5 mL of dry THF were added dropwise and the resulting mixture was stirred for 12 h at room temperature. The solvent was removed under vacuum and the sticky material was redissolved in CH_2Cl_2 (20 mL) and washed with water (20 mL). The water phase was extracted three times with 20 mL of CH_2Cl_2 and the organic phases were combined, dried over $MgSO_4$, and the solvent was evaporated. The resulting residue was recrystallized from methanol to yield a light-yellow powder of **^{pr}LH** in Yield: 330mg (57 %). Elemental analysis: Calc. for $C_{18}H_{26}N_2O$: C 76.78, H 9.82, N 8.53; Found: C 73.79, H 9.39, N 7.39. Calc.with MeOH: C 73.29, H 10.06, N 7.77. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 11.3 (s, 1H, OH), 7.40 (d, 2.4 Hz, 1H, Ar), 7.25 (d, 2.4 Hz, 1H, Ar), 6.39 (d, 0.6 Hz, 1H, pz), 4.01 (t, 7.05 Hz, 2H, CH_2), 2.33 (d, 0.6 Hz, 3H, CH_3), 1.89 (q, 7.3 Hz, 2H, CH_2), 1.48 (s, 9H, ^{t}*Bu*), 1.34 (s, 9H, ^{t}*Bu*), 0.94 (t, 7.5 Hz, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ 152.64, 151.00, 140.28, 138.80, 136.23, 123.41, 120.78, 116.12, 102.03, 50.35, 35.95, 34.19, 31.64, 29.65, 23.33, 11.12, 10.99. M.p. 96 °C. M.S ES(+): m/z 329 (MH^+). IR (ZnSe): ν, 2953, 1566, 1605, 1461, 1377, 1354 cm^{-1}.

[Cu^{Me}L$_2$] (2).

To a solution of **^{Me}LH** (50 mg, 0.66 mmol, 2 eq.) in methanol (5 mL), was added a solution of $Cu(BF_4)_2 \cdot 6H_2O$ (30 mg, 0.083 mmol, 1eq.) in methanol (5 mL). Addition of Et_3N (24 μL, 2eq.) to the reaction mixture caused an immediate purple microcrystalline precipitate to be formed. After a few minutes, the solid was collected by filtration. The purple powder was recrystallized by slow evaporation of DMF, and collected in 68 % yield. M.S ES(+): m/z 634 (MH^+). Elemental analysis: Calc. for $C_{38}H_{54}CuN_4O_2$: C 68.9, H 8.22, N 8.78; Found: C 68.29, H 7.95, N 8.78. UV/vis (CH_2Cl_2): λ_{max}/nm (ε/M^{-1} cm^{-1}): 520 (787), 755 (350). IR(ZnSe) : ν 2955, 1553, 1430, 1299, 1254 cm^{-1}.

[Cu^{Pr}L$_2$] (3).

The **^{Pr}LH** (50 mg, 0.152 mmol 2 eq.) in methanol (5 mL), and the $Cu(BF_4)_2 \cdot 6H_2O$ (26 mg, 0.076 mmol, 1eq.) in methanol (5 mL) were used as described above. Addition of Et_3N (2eq. 24μL) to the reaction mixture caused an immediate purple microcrystalline precipitate to be formed. After a few minutes, the solid was collected by filtration. The purple powder was recrystallized by slow evaporation in DMF. After a week, large purple rectangles crystals of **3** suitable for X-ray crystallography were collected in 73 % yield. M.S ES(+): m/z 718 (MH$^+$). Elemental analysis: Calc. for $C_{42}H_{62}CuN_4O_2$: C 70.21, H 8.70, N 7.80; Found: C 69.82, H 8.50, N 7.78. UV/vis (CH_2Cl_2): λ_{max}/nm (ε/M^{-1} cm^{-1}): 535 (737), 745 (300). IR(ZnSe) : v 2919, 1605, 1514, 1452, 1302 cm^{-1}.

Physical methods

Elemental analyses of the compounds isolated in these studies were accomplished in the University of Bar Ilan. EI mass spectra were recorded on a Q-Tof micro (UK)-micromass-waters spectrometer. 1H-spectra were recorded on a Bruker DPX300 NMR spectrometer, some of the materials were recorded on 13C NMR 75 MHz. EPR spectra were recorded on a Bruker X-band EMX spectrometer; all spectra were calibrated using DPPH radical as an internal standard, and g-values were calculated accordingly. Frozen solution EPR spectra were recorded at 77 K using a quartz cold-finger dewar (Wilmad WG-816-Q) filled with liquid nitrogen. All EPR simulations spectra were performed using Bruker Simfonia software package. UV/Vis spectra were recorded on a Varian Cary 5000 UV/Vis/NIR spectrophotometer.

The measurements were carried out using a quartz cuvette with optical pathlength of 0.1 cm. IR spectra were recorded on a Nicolet iS10 FT-IR spectrometer using ATR accessory on ZnSe crystal for powder samples pressed. Cyclic voltammetry measurements were carried out using a Bio Logic SAS Sp-150 potentiostat. For all electrochemical experiments, the CH_2Cl_2 was freshly distilled under dinitrogen from calcium hydride. The cyclic voltammogram of each compound (1 mM) in CH_2Cl_2 containing $[NBu_4][PF_6]$ (0.15 M) as the background electrolyte was recorded under dinitrogen at room temperature using a Pt working electrode; a Pt wire secondary electrode, and an Ag/AgCl reference electrode. The cyclic voltammogram of each compound was referenced to the Fc$^+$/Fc couple that was used as an internal standard. When necessary, to avoid overlapping redox couples, the $[Fe(Cp^*)_2]$+/$[Fe(Cp^*)_2]$ couple was used as the internal reference and the potentials of the redox process(es) observed were referenced to that of the Fc+/Fc couple by an independent calibration (Δ*E*1/2 (Fc+/Fc *vs.* 60 [Fe(Cp*)2]+/[FeCp*2], = 0.526 V). Controlled potential electrolysis measurements were performed using an Bio Logic SAS Sp-150 potentiostat. A three electrodes configuration was used in the cell, comprising a Pt gauze working electrode, a Pt wire secondary electrode contained in a fritted PTFE sleeve, and 65 a saturated Ag/AgCl. The potential at the working electrode was controlled by a Bio Logic SAS Sp-150 potentiostat. X-ray crystallography: Single crystal X-ray diffraction data for **3** were collected at 120K on a Bruker SMART 6000 CCD area detector diffractometer equipped with a Cryostream (Oxford Cryosystems) open-flow nitrogen cryostat using graphite-monochromated

Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct method and refined by full-matrix least-squares on F^2 for all data using SHELXTL[1] and OLEX2[2] software. All non-disordered non-H atoms were refined with anisotropic atomic displacement parameters, the disordered t-Bu group was refined isotropically with fixed SOFs 0.6 and 0.4. All hydrogen atoms were placed in the calculated positions and refined in "riding" mode. The crystallographic data are listed in Table S1. The largest peak on the residual map is located in the vicinity of disordered t-Bu group. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC- 846432

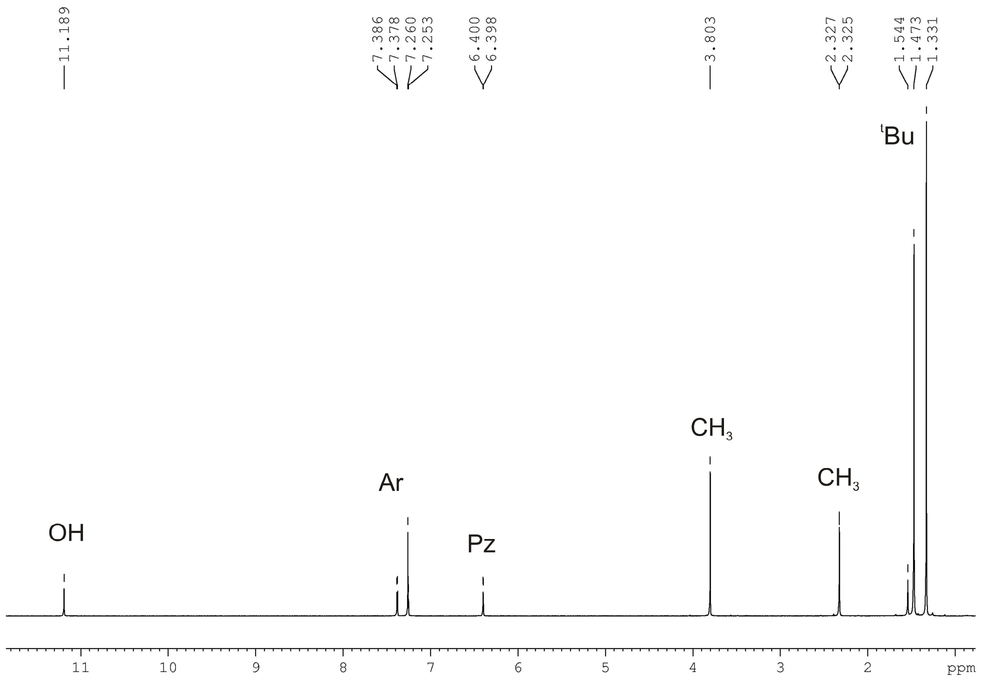


Fig. S1 ^{1}H NMR (300 MHz) spectrum of $^{\mathbf{Me}}$**LH** in $CDCl_3$ at room temperature

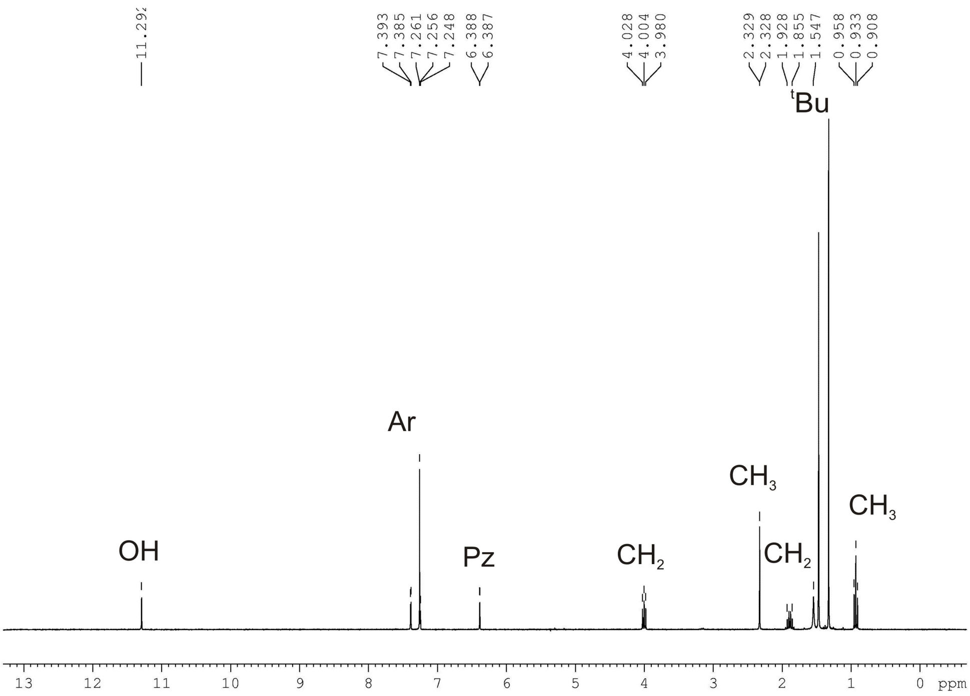


Fig. S2 ^{1}H NMR (300 MHz) spectrum of ^{Pr}**LH** in $CDCl_3$ at room temperature.

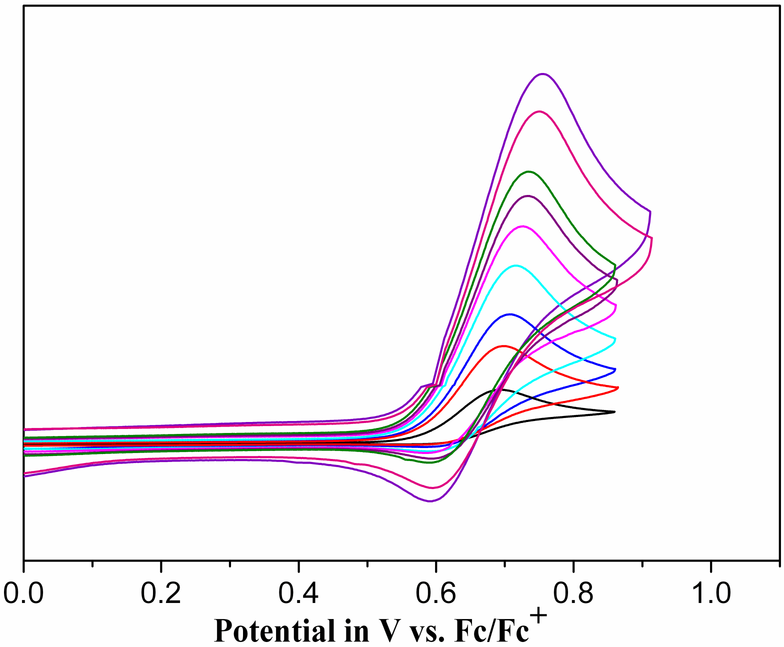


Fig. S3 Cyclic voltammograms of ^{Me}**LH** (~1 mM) in CH_2Cl_2 at 298 K containing $[NBu_4][PF_6]$ (0.2 M) as supporting electrolyte, at scan rates of 20-1000 mV s^{-1}.

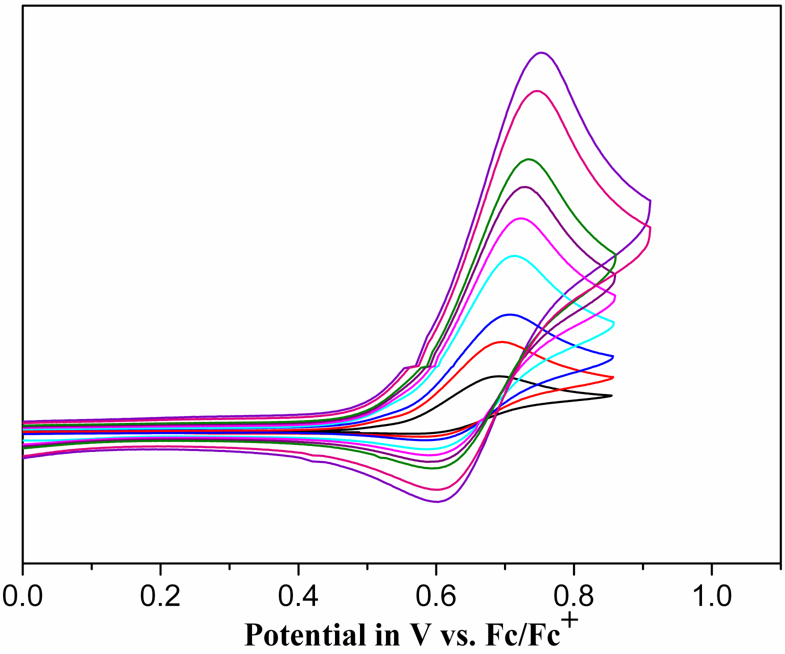


Fig. S4 Cyclic voltammograms of ^{Pr}**LH** (~1 mM) in CH_2Cl_2 at 298 K containing $[NBu_4][PF_6]$ (0.2 M) as supporting electrolyte, at scan rates of 20-1000 mV s^{-1}.

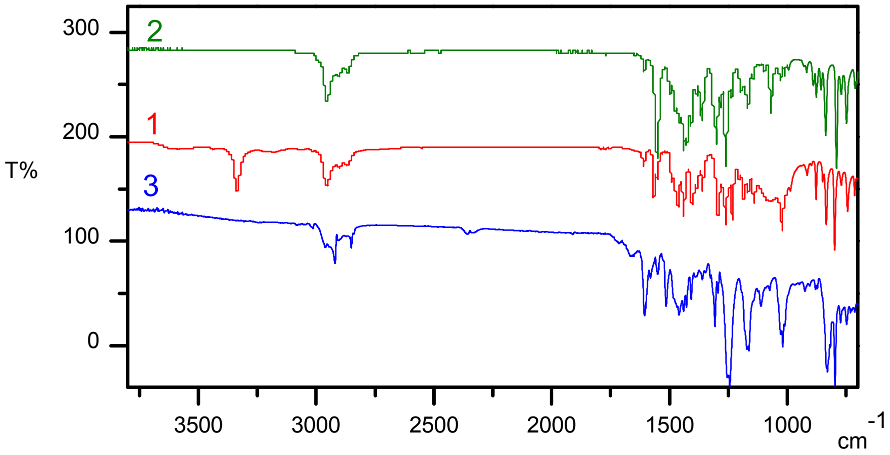


Fig. S5 Solid state IR spectra of **1**, **2**, and **3**.

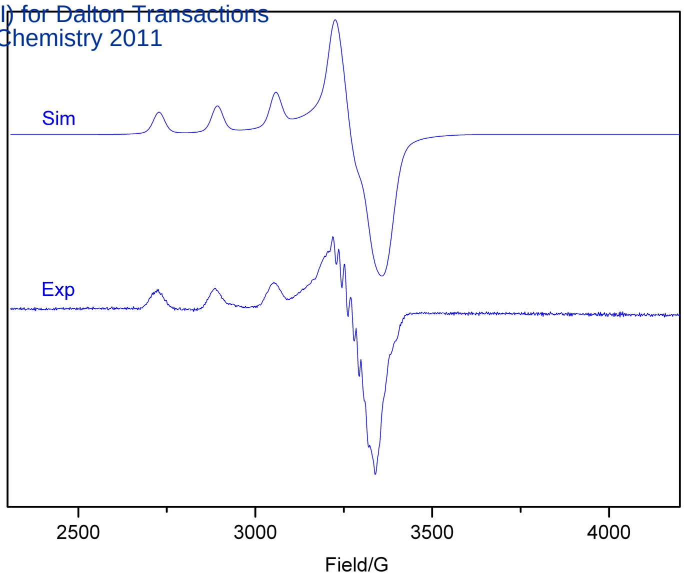


Fig. S6 X-band EPR spectra of **3** (*ca.* 1 mM) in CH_2Cl_2 recorded at 77 K and its simulated spectrum.. Experimental parameters: center field: 3284.21 G; modulation frequency: 100 KHz; modulation amplitude: 5 G; receiver gain: $1.12 \cdot 10^{-5}$; conversion time: 81.92 ms; time constant: 5.12 ms; Sweep Time : 83.88 s. Microwave power: 6.3 mW. Simulation parameters: $g_x = 2.027$, $g_y = 2.058$, $g_z = 2.258$; $A_{zz}\{^{63,65}Cu\} = 160$ G; line shape: Lorentzian/Gaussian: 0.5; linewidth: 40 G.

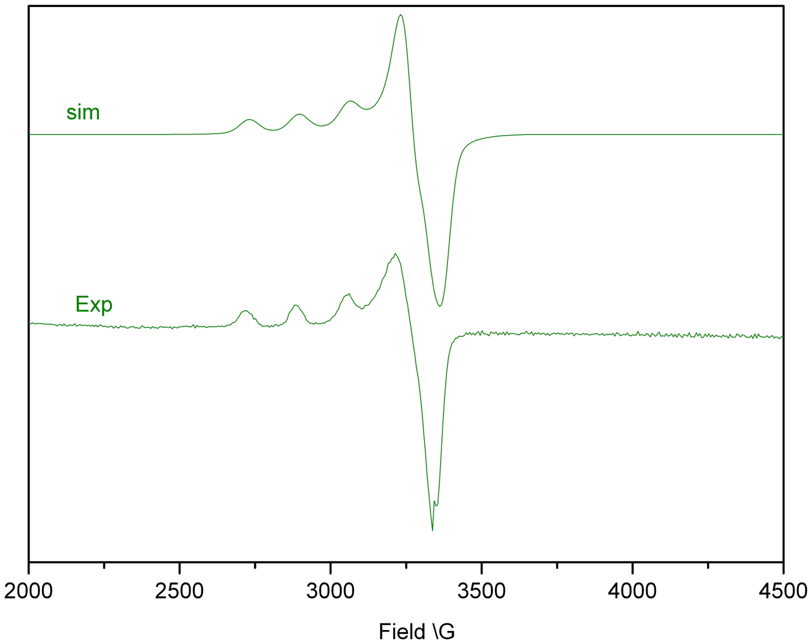


Fig. S7 X-band EPR spectra of **2** (*ca.* 1 mM) in CH_2Cl_2 recorded at 77 K and its simulated spectrum. Experimental parameters: center field: 3000 G; modulation frequency: 100 KHz; modulation amplitude: 5 G; receiver gain: $1 \cdot 10^{-5}$; conversion time: 81.92 ms; time constant: 1.28 ms; ST: 83.88 s. Microwave power: 6.3mW. Simulation parameters: $g_x = 2.027$, $g_y = 2.058$, $g_z = 2.258$; $A_{zz}\{^{63,65}Cu\} = 165$ G; line shape: Lorentzian/Gaussian: 0.5; linewidth: 40 G.

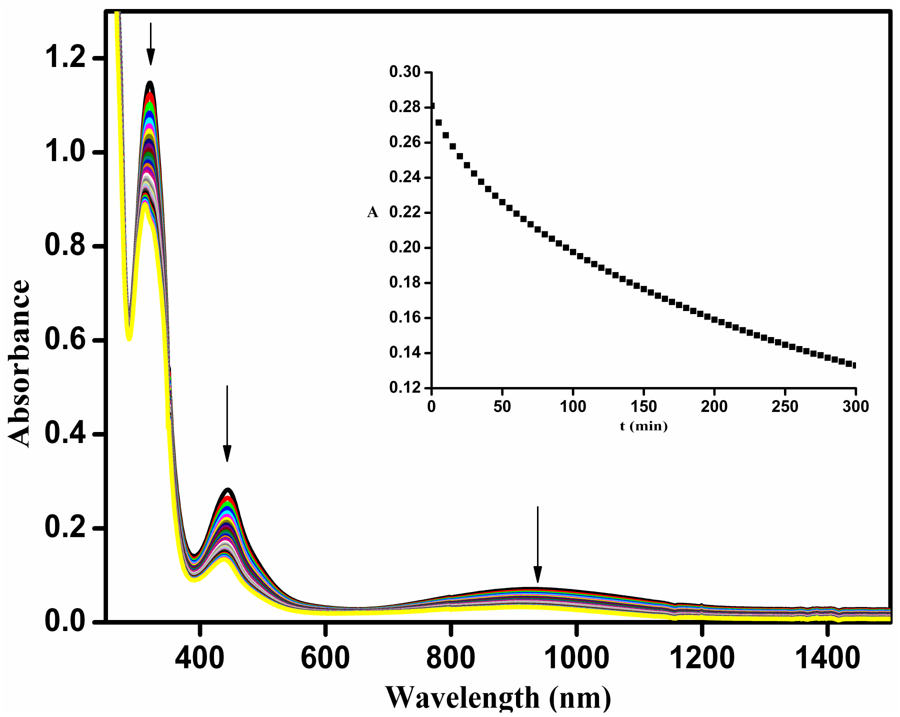


Fig. S8 Decay of electrogenerated **1**$^+$ in CH_2Cl_2 (0.15 M $TBAPF_6$). The insert represents the decay pattern at $T = 298$ K, $l = 1.000$ mm, $\lambda = 442$ nm.

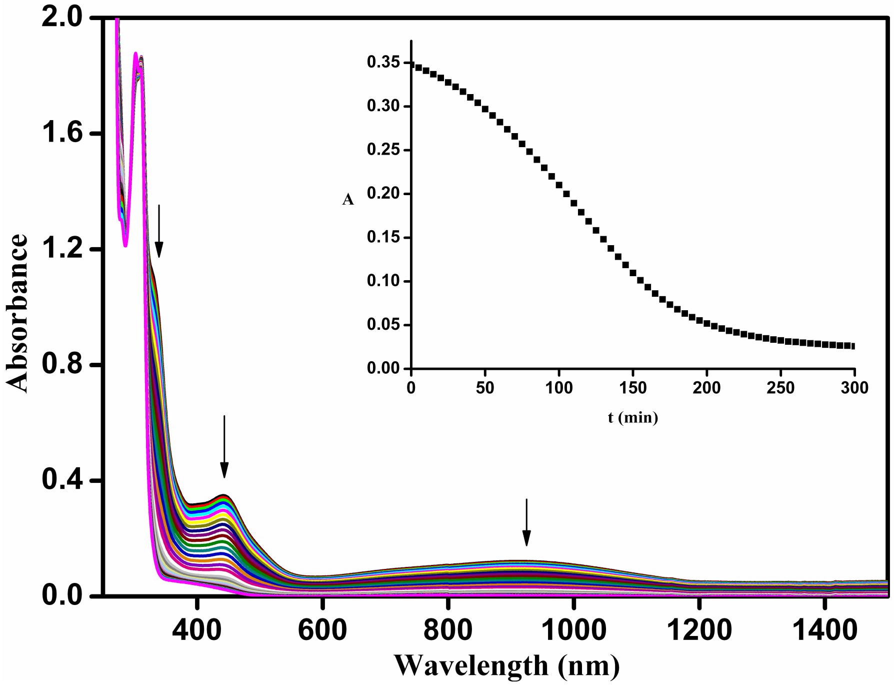


Fig. S9 Decay of electrogenerated **2**$^+$ in CH_2Cl_2 (0.15 M $TBAPF_6$). The insert represents the decay pattern at $T = 298$ K, $l = 1.000$ mm, $\lambda = 438$ nm

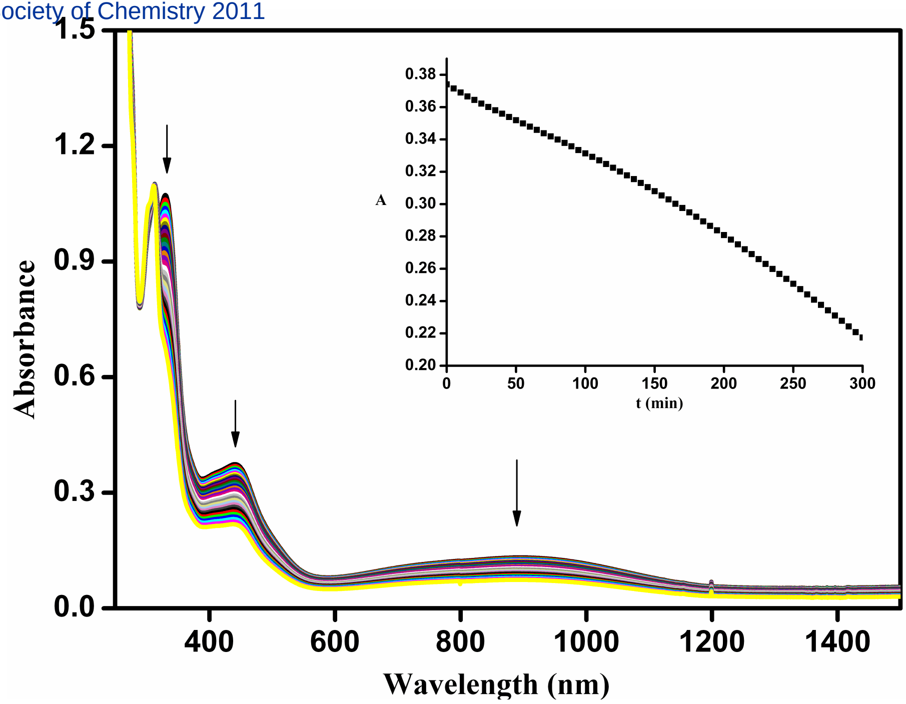


Fig. S10 Decay of electrogenerated **3**$^+$ in CH_2Cl_2 (0.15 M $TBAPF_6$). The insert represents the decay pattern at $T = 298$ K, $l = 1.000$ mm, $\lambda = 442$ nm.

Table S1 Crystal data and structure refinement for **3**

Empirical formula	$C_{42}H_{62}CuN_4O_2$
Formula weight	718.50
Temperature / K	-153
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å, b / Å, c / Å	25.4688(7), 9.5148(3), 16.9516(5)
α/°, β/°, γ/°	90.00, 91.368(10), 90.00
Volume / $Å^3$	4106.7(2)
Z	4
ρ_{calc} / mg mm^{-3}	1.162
μ / mm^{-1}	0.569
F(000)	1548
Crystal size / mm^3	0.58 × 0.2 × 0.15
2Θ range for data collection	3.2 to 56°
Index ranges	$-33 \le h \le 33, -12 \le k \le 12, -22 \le l \le 22$
Reflections collected	46126
Independent reflections	9913[R(int) = 0.0363]
Data/restraints/parameters	9913/0/458
Goodness-of-fit on F^2	1.084
Final R indexes [I>2σ (I)]	$R_1 = 0.0514$, $wR_2 = 0.1342$
Final R indexes [all data]	$R_1 = 0.0668$, $wR_2 = 0.1455$
Largest diff. peak/hole / e $Å^{-3}$	1.036/-0.553

Table S2 Selected bond lengths/Å and angles/° for **3**

	3
Cu1- O1	1.8829(16)
Cu1- O2	1.8783(16)
Cu1- N1	1.956(2)
Cu1- N3	1.9538(19)
O1-Cu1-N1	91.25(8)
O1- Cu1- N3	154.11(8)
O2- Cu1- O1	88.15(7)
O2- Cu1- N1	150.92(8)
O2- Cu1- N3	89.22(7)
N3- Cu1- N1	103.24(8)
C1-O1-Cu1	126.54(15)
C31-O2-Cu1	127.36(14)
N2-N1-Cu1	128.26(18)
C15-N1-Cu1	124.98(17)

References

1 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112.

2 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.