

Supporting Information

Experimental Section

All synthetic work was performed under standard Schlenk techniques und an atmosphere of dry nitrogen. (^tBu₂bipy)PtCl₂ was prepared according to ref. 1. The thiocoumarine was obtained from Aldrich and the other coumarines from ABCR. Solvents were dried by standard procedures and degassed by saturation with nitrogen prior to use. Infrared spectra were obtained on a Perkin Elmer Paragon 1000 PC FT-IR instrument. ¹H (250.13 MHz), ¹³C (62.90 MHz) and ³¹P-NMR spectra (101.26 MHz) were recorded on a Bruker AC 250 spectrometer as CDCl₃ or CD₂Cl₂ solutions at 303K. The spectra were referenced to the residual protonated solvent (¹H), the solvent signal itself (¹³C) or external H₃PO₄ (³¹P). The assignment of ¹³C NMR signals was aided by HSQC and HMBC experiments. UV/vis spectra were obtained on an Omega 10 spectrometer from Bruins Instruments in HELMA quartz cuvettes whith 1 cm optical path lengths. Elemental analyses (C,H,N) were performed at in-house facilities. Electrochemical work was performed on a BAS CV50 potentiostat in a home-built vacuum tight one-compartment cell using Pt or glassy carbon disk electrodes from BAS as the working electrode, a platinum spiral as the counter electrode and a silver spiral as a pseudo-reference electrode. Each of the spiral-shaped electrodes was welded to Vycon wire and sealed into a glass tube. Counter and reference electrodes are introduced into the cell by appropriate fittings in the side-wall and sealed via a Quickfit screw. The design of the spectroelectrochemical cell follows that of Hartl et al.² CH₂Cl₂ and 1,2-C₂H₄Cl₂ for electrochemical use were of Burdick&Jackson brand (Fluka) and were distilled from CaH₂, deoxygenated by saturation with argon and briefly stored over molecular sieves. Potential calibration was performed by adding ferrocene (**1**, **2**) or decamethylferrocene (**3**) as an internal standard to the analyte solution. The amount of the reference system was adjusted until its peak currents were comparable to those of the analyte. Potentials are given against the ferrocene/ferrocenium couple. **Cautionary Note:** 1,2-Dichloroethane (DCE) is highly toxic and a suspected carcinogen and should be handled with care.

Emission and excitation spectra at 77 K were measured with a steady-state fluorescence spectrometer (Jobin Yvon Fluorolog 3). For decay time measurements, the sample was excited with a pulsed diode laser (PicoQuant PDL 800-B) with a pulse width of about 500 ps and an excitation wavelength of 375 nm, the decay times were registered using a FAST Comtec multichannel scaler PCI card with a time resolution of 250 ps. Emission quantum yields at 77 K were determined with a commercially available system for the measurements of absolute quantum yields (Hamamatsu Photonics C9920-02).

Synthesis of complex 1: 4-Methyl-7-thiocoumarine (108 mg, 0.561 mmol) and KOH (158 mg, 2.81 mmol) were suspended in 30 mL of methanol. After stirring for 5 min the resulting clear solution was added dropwise to a suspension of (^tBu₂bipy)PtCl₂ (100 mg, 0.187 mmol) in 15 mL of acetone. The mixture was stirred at r.t. for 2 h and then filtered. The residue was washed with 5 mL of methanol and dried in vacuum to give **1** as orange powder. (119 mg, 0.140 mmol, 75%).

¹H NMR (300 MHz, 298 K, CDCl₃), δ 9.64 [2H, d, 2-*H* (bipy), ³J_{H-H} = 6.11 Hz], 8.05 [2H, d, 5-*H* (bipy), ⁴J_{H-H} = 1.99 Hz], 7.72 [2H, d, 8-*H* (7-thiocoum) ⁴J_{H-H} = 1.85 Hz], 7.56 [2H, dd, 3-*H* (bipy), ³J_{H-H} = 6.11 Hz, ⁴J_{H-H} = 1.99 Hz], 7.47 [2H, dd, 6-*H* (7-thiocoum), ³J_{H-H} = 8.43 Hz, ⁴J_{H-H} = 1.85 Hz], 7.14 [2H, d, 5-*H* (7-thiocoum), ³J_{H-H} = 8.43 Hz], 6.00 [2H, q, 3-*H* (7-

thiocoum), $^4J_{\text{H-H}} = 1.17$ Hz], 2.31 [6H, d, *Me-H* (7-thiocoum), $^4J_{\text{H-H}} = 1.17$ Hz], 1.47 [18H, s, *t-Bu-H* (bipy)].

^{13}C NMR (400 MHz, 298 K, CDCl_3) δ 164.54 [s, 4-*C* (bipy)], 161.54 [s, 2-*C* (7-thiocoum)] 156.26 [s, 6-*C* (bipy)], 152.82 [s, 4-*C* (7-thiocoum)], 152.74 [s, 8*a*-*C* (7-thiocoum)] 152.50 [s, 7-*C* (7-thiocoum)], 148.99 [s, 2-*C* (bipy)], 127.32 [s, 6-*C* (7-thiocoum)], 124.57 [s, 3-*C* (bipy)], 122.63 [s, 5-*C* (7-thiocoum)], 119.49 [s, 5-*C* (bipy)], 118.49 [s, 8-*C* (7-thiocoum)], 114.92 [s, 4*a*-*C* (7-thiocoum)], 111.33 [s, 3-*C* (7-thiocoum)], 35.88 [s, C_{quat} /*t*-Bu (bipy)], 30.16 [s, CH_3 /*t*-Bu (bipy)], 18.47 [s, *Me-C* (7-thiocoum)].

Synthesis of complex 2: Umbelliferone (7-hydroxy-4-methylcoumarine) (55 mg, 0.314 mmol) and KO^tBu (35 mg, 0.314 mmol) were treated with 10 mL of THF and 3 mL of methanol. The suspension was stirred for 30 min and added slowly to a suspension of ($^t\text{Bu}_2\text{bipy}$) PtCl_2 (84.0 mg, 0.157 mmol) in 20 mL of CH_2Cl_2 . The mixture was refluxed for 18 h and cooled to r.t. whereupon a yellow solid precipitated from the brown solution. After filtration and washing with 3 mL of methanol the residue was dried in vacuum to give **2** as a yellow powder. All volatiles of the filtrate were removed in vacuum and the crude product was suspended in 5 mL of methanol. After filtration the residue was dried in vacuum and another fraction of **2** was obtained (combined yield: 103 mg, 0.127 mmol, 81%).

^1H -NMR (400 MHz, 298 K, CD_2Cl_2) δ 8.72 [2H, d, 2-*H* (bipy), $^3J_{\text{H-H}} = 6.12$ Hz], 7.98 [2H, d, 5-*H* (bipy), $^4J_{\text{H-H}} = 1.88$ Hz], 7.54 [2H, dd, 3-*H* (bipy), $^3J_{\text{H-H}} = 6.12$ Hz, $^4J_{\text{H-H}} = 1.88$ Hz], 7.27 [2H, d, 5-*H* (7-oxocoum), $^4J_{\text{H-H}} = 8.80$ Hz] 7.12 [2H, d, 8-*H* (7-oxocoum), $^3J_{\text{H-H}} = 2.36$ Hz] 7.09 [2H, dd, 6-*H* (7-oxocoum), $^3J_{\text{H-H}} = 8.80$ Hz, $^4J_{\text{H-H}} = 2.36$ Hz], 5.79 [2H, s(br), 3-*H* (7-oxocoum)], 2.29 [6H, s(br), *Me-H* (7-oxocoum)], 1.45 [18H, s, *t-Bu-H* (bipy)].

^{13}C -NMR (600 MHz, CD_2Cl_2) δ (ppm): 172.86 [s, 7-*C* (7-oxocoum)], 165.19 [s, 4-*C* (bipy)], 162.37 [s, 2-*C* (7-oxocoum)], 157.24 [s, 6-*C* (bipy)], 155.97 [s, 8*a*-*H* (7-oxocoum)], 153.67 [s, 4-*C* (7-oxocoum)], 148.95 [s, 2-*C* (bipy)], 124.93 [s, 5-*C* (7-oxocoum)], 124.72 [s, 3-*C* (bipy)], 120.01 [s, 5-*C* (bipy)], 117.36 [s, 6-*C* (7-oxocoum)], 110.15 [s, 4*a*-*C* (7-oxocoum)], 108.43 [s, 3-*C* (7-oxocoum)], 105.73 [s, 8-*C* (7-oxocoum)], 36.30 [s, C_{quat} /*t*-Bu (bipy)], 30.25 [s, CH_3 /*t*-Bu (bipy)], 18.75 [s, *Me-C* (7-oxocoum)]. CHN analysis for $\text{C}_{38}\text{H}_{38}\text{N}_2\text{O}_6\text{Pt}$: calculated (measured): C 56.08 (56.39), H 4.71 (4.94), N 3.42 (3.19).

Synthesis of complex 3: Esculetin (6,7-dihydroxy-4-methylcoumarine) (193 mg, 0.338 mmol) and KO^tBu (38 mg, 0.338 mmol) were treated with 10 mL THF and 3 mL of methanol. The suspension was stirred for 30 min and then added slowly to a suspension of ($^t\text{Bu}_2\text{bipy}$) PtCl_2 (151 mg, 0.282 mmol) in 20 mL of CH_2Cl_2 . The mixture was refluxed for 18 h. After cooling down to r. t. a purple solid precipitated from the red solution. After filtration and washing with 3 mL of methanol the residue was dried in vacuum to give **3** as a purple powder. All volatiles of the filtrate were removed in vacuum and the crude product was suspended in 8 mL of methanol. After filtration the residue was dried in vacuum and another fraction of **3** was obtained (combined yield: 146 mg, 0.223 mmol, 79%).

^1H -NMR (600 MHz, 298 K, CDCl_3) δ 9.14-9.08 [2H, m, 2-*H* and 2'-*H* (bipy)], 7.83 [2H, s(br), 5-*H* and 5'-*H* (bipy)], 7.54-7.48 [2H, m, 3-*H* and 3'-*H* (bipy)], 6.87 [1H, 5-*H* (6,7-dioxocoum)], 6.69 [1H, d, 8-*H* (6,7-dioxocoum)], 5.94 [2H, s(br), 3-*H* (6,7-dioxocoum)], 2.33 [6H, s(br), *Me-H* (6,7-dioxocoum)], 1.462 and 1.459 [18H, s, *t-Bu-H* and *t-Bu*'-*H* (bipy)].

^{13}C -NMR (600 MHz, CDCl_3) δ (ppm): 165.57 [s, 7-*C* (6,7-dioxocoum)], 163.46 and 163.40 [s, 4-*C* and 4'-*C* (bipy)], 163.36 [s, 2-*C* (6,7-dioxocoum)], 160.65 [s, 6-*C* (6,7-dioxocoum)], 156.03 and 155.79 [s, 6-*C* and 6'-*C* (bipy)], 153.39 [s, 8*a*-*C* (6,7-dioxocoum)], 149.28 and 149.23 [s, 2-*C* and 2'-*C* (bipy)], 148.28 [s, 3-*C* (6,7-dioxocoum)], 124.23 and 124.05 [s, 3-*C* and 3'-*C* (bipy)], 119.21 and 119.18 [s, 5-*C* and 5'-*C* (bipy)], 110.10 [s, 4*a*-*C* (6,7-

dioxocoum)], 108.21 [s, 3-C (6,7-dioxocoum)], 105.87 [s, 5-C (6,7-dioxocoum)], 102.14 [s, 8-C (6,7-dioxocoum)], 35.93 [s(br), C_{quat}/t-Bu (bipy)], 30.26 [s (br), CH₃/t-Bu (bipy)], 19.12 [s, Me-C (6,7-dioxocoum)]. CHN analysis for C₂₈H₃₀N₂O₄Pt×2H₂O: calculated (measured): C 48.76 (49.06), H 4.97 (4.78), N 4.06 (4.07).

Crystals of complexes **1** and **2** were obtained by layering concentrated CH₂Cl₂ solutions with n-hexane.

Calculations

The electronic structures of the complexes **1** and **3** were calculated by density functional theory (DFT) methods using the Gaussian 09³ program package. Low-lying singlet excited states were calculated by time-dependent DFT (TD-DFT) at the optimized ground-state geometry.

Gaussian calculations employed the hybrid Perdew, Burke and Ernzerhof^{4,5} (PBE0) exchange and correlation functional. For H, C, N, O and S atoms either 6-311g(d) polarized triple - ζ basis sets⁶ for geometry optimization or cc-pvdz correlation consistent polarized valence double ζ basis sets⁷ (TD-DFT) were used, together with quasirelativistic effective core pseudopotentials and corresponding optimized set of basis functions for Pt.^{8,9} The solvent was described by the polarizable continuum model (PCM).¹⁰

Table S1 Bond lengths [Å] for complex **1** and the three independent molecules within the unit cell of **2**.

1		2		2'		2''	
Pt(1)-S(1)	2.2913(14)	Pt(1)-O(1)	2.009(6)	Pt(2)-O(7)	2.013(6)	Pt(3)-O(10)	2.018(6)
Pt(1)-S(2)	2.2929(15)	Pt(1)-O(4)	2.026(8)	Pt(2)-O(7)#1	2.013(6)	Pt(3)-O(10)#2	2.018(6)
Pt(1)-N(1)	2.051(5)	Pt(1)-N(2)	1.992(7)	Pt(2)-N(3)#1	1.997(10)	Pt(3)-N(4)#2	1.994(6)
Pt(1)-N(2)	2.052(5)	Pt(1)-N(1)	2.012(6)	Pt(2)-N(3)	1.997(10)	Pt(3)-N(4)	1.994(6)
S(1)-C(19)	1.742(6)	O(1)-C(19)	1.295(11)	O(7)-C(48)	1.296(12)	O(10)-C(67)	1.306(10)
S(2)-C(29)	1.752(5)	O(4)-C(29)	1.381(18)				
O(1)-C(23)	1.378(8)	O(2)-C(23)	1.381(11)	O(8)-C(52)	1.402(12)	O(11)-C(71)	1.381(11)
O(1)-C(25)	1.402(8)	O(2)-C(28)	1.407(16)	O(8)-C(57)	1.381(14)	O(11)-C(76)	1.403(14)
O(2)-C(25)	1.202(9)	O(3)-C(28)	1.208(17)	O(9)-C(57)	1.237(16)	O(12)-C(76)	1.195(16)
O(3)-C(33)	1.361(9)	O(5)-C(33)	1.38(2)				
O(3)-C(35)	1.374(17)	O(5)-C(38)	1.37(3)				
O(4)-C(35)	1.166(19)	O(6)-C(38)	1.16(3)				
N(1)-C(1)	1.340(8)	N(2)-C(10)	1.315(12)				
N(1)-C(5)	1.357(8)	N(2)-C(6)	1.334(10)				
N(2)-C(6)	1.352(8)	N(1)-C(5)	1.364(11)	N(3)-C(39)	1.328(13)	N(4)-C(58)	1.339(10)
N(2)-C(10)	1.374(9)	N(1)-C(1)	1.332(12)	N(3)-C(43)	1.33(2)	N(4)-C(62)	1.348(11)
C(1)-C(2)	1.384(9)	C(9)-C(10)	1.393(14)				
C(2)-C(3)	1.389(9)	C(8)-C(9)	1.384(14)				
C(3)-C(4)	1.388(9)	C(7)-C(8)	1.388(14)				
C(3)-C(11)	1.538(9)	C(8)-C(15)	1.570(14)				
C(4)-C(5)	1.386(9)	C(6)-C(7)	1.381(13)				
C(5)-C(6)	1.495(8)	C(5)-C(6)	1.460(12)	C(39)-C(39)#1	1.508(18)	C(58)-C(58)#2	1.503(13)
C(6)-C(7)	1.371(9)	C(4)-C(5)	1.386(13)	C(39)-C(40)	1.384(17)	C(58)-C(59)	1.355(12)
C(7)-C(8)	1.402(10)	C(3)-C(4)	1.398(15)	C(40)-C(41)	1.42(3)	C(59)-C(60)	1.402(13)
C(8)-C(9)	1.382(10)	C(2)-C(3)	1.389(15)	C(41)-C(42)	1.370(19)	C(60)-C(61)	1.373(12)
C(8)-C(15)	1.518(11)	C(3)-C(11)	1.530(15)	C(41)-C(44)	1.49(2)	C(60)-C(63)	1.520(13)
C(9)-C(10)	1.380(11)	C(1)-C(2)	1.349(13)	C(42)-C(43)	1.378(19)	C(61)-C(62)	1.374(13)
C(11)-C(12)	1.519(13)	C(15)-C(16)	1.550(18)				
C(11)-C(13)	1.524(14)	C(15)-C(17)	1.582(17)				
C(11)-C(14)	1.533(11)	C(15)-C(18)	1.466(18)				
C(15)-C(16)	1.531(19)	C(11)-C(12)	1.466(19)	C(44)-C(45)	1.48(4)	C(63)-C(64)	1.518(17)
C(15)-C(17)	1.561(13)	C(11)-C(13)	1.50(2)	C(44)-C(46)	1.49(3)	C(63)-C(65)	1.51(2)
C(15)-C(18)	1.469(16)	C(11)-C(14)	1.499(18)	C(44)-C(47)	1.47(2)	C(63)-C(66)	1.479(17)
C(19)-C(20)	1.398(9)	C(19)-C(20)	1.427(13)	C(48)-C(49)	1.409(15)	C(67)-C(68)	1.412(12)
C(19)-C(24)	1.412(9)	C(19)-C(24)	1.407(12)	C(48)-C(53)	1.359(15)	C(67)-C(72)	1.414(13)
C(20)-C(21)	1.386(9)	C(20)-C(21)	1.365(14)	C(49)-C(50)	1.368(16)	C(68)-C(69)	1.360(13)
C(21)-C(22)	1.406(9)	C(21)-C(22)	1.415(14)	C(50)-C(51)	1.359(16)	C(69)-C(70)	1.407(13)
C(22)-C(23)	1.386(9)	C(22)-C(23)	1.403(13)	C(51)-C(52)	1.417(17)	C(70)-C(71)	1.389(13)
C(22)-C(27)	1.442(9)	C(22)-C(25)	1.432(15)	C(51)-C(54)	1.432(17)	C(70)-C(73)	1.434(15)
C(23)-C(24)	1.385(9)	C(23)-C(24)	1.378(13)	C(52)-C(53)	1.369(15)	C(71)-C(72)	1.363(12)
C(25)-C(26)	1.435(10)	C(27)-C(28)	1.41(2)	C(56)-C(57)	1.46(2)	C(75)-C(76)	1.409(19)
C(26)-C(27)	1.359(10)	C(25)-C(27)	1.327(17)	C(54)-C(56)	1.352(19)	C(73)-C(75)	1.348(19)
C(27)-C(28)	1.515(10)	C(25)-C(26)	1.488(17)	C(54)-C(55)	1.53(2)	C(73)-C(74)	1.50(2)
C(29)-C(30)	1.3902	C(29)-C(30)	1.374(19)				
C(29)-C(34)	1.3891	C(29)-C(34)	1.412(18)				
C(30)-C(31)	1.3902	C(30)-C(31)	1.36(2)				
C(31)-C(32)	1.3898	C(31)-C(32)	1.40(3)				
C(32)-C(33)	1.3902	C(32)-C(33)	1.39(3)				
C(32)-C(37)	1.474(13)	C(32)-C(35)	1.47(3)				
C(33)-C(34)	13.895	C(33)-C(34)	1.36(3)				
C(35)-C(36)	1.42(3)	C(37)-C(38)	1.46(3)				
C(36)-C(37)	1.304(18)	C(35)-C(37)	1.35(3)				
C(37)-C(38)	1.49(3)	C(35)-C(36)	1.46(3)				

Table S2 Bond Angles [°] for complex **1** and the three independent molecules of **2**.

1		2		2'		2''	
S(1)-Pt(1)-S(2)	88.35(5)	O(1)-Pt(1)-O(4)	91.3(3)	O(7)-Pt(2)-O(7)#1	93.6(3)	O(10)-Pt(3)-O(10)#2	96.7(2)
S(1)-Pt(1)-N(1)	175.40(13)	O(1)-Pt(1)-N(2)	174.1(3)	O(7)-Pt(2)-N(3)#1	172.3(3)	O(10)-Pt(3)-N(4)#2	171.6(2)
S(1)-Pt(1)-N(2)	96.85(14)	O(1)-Pt(1)-N(1)	93.9(3)	O(7)-Pt(2)-N(3)	93.0(4)	O(10)-Pt(3)-N(4)	91.5(3)
S(2)-Pt(1)-N(1)	96.26(13)	O(4)-Pt(1)-N(2)	94.1(3)	O(7)#1-Pt(2)-N(3)#1	93.0(4)	O(10)#2-Pt(3)-N(4)#2	91.5(3)
S(2)-Pt(1)-N(2)	174.75(14)	O(4)-Pt(1)-N(1)	174.6(3)	O(7)#1-Pt(2)-N(3)	172.3(3)	O(10)#2-Pt(3)-N(4)	171.6(2)
N(1)-Pt(1)-N(2)	78.55(18)	N(1)-Pt(1)-N(2)	80.8(3)	N(3)-Pt(2)-N(3)#1	80.8(4)	N(4)-Pt(3)-N(4)#2	80.4(3)
Pt(1)-S(1)-C(19)	106.0(2)	Pt(1)-O(1)-C(19)	123.6(6)	Pt(2)-O(7)-C(48)	125.0(6)	Pt(3)-O(10)-C(67)	127.2(5)
Pt(1)-S(2)-C(29)	102.58(18)	Pt(1)-O(4)-C(29)	120.4(7)				
C(23)-O(1)-C(25)	121.0(5)	C(23)-O(2)-C(28)	119.9(9)	C(52)-O(8)-C(57)	119.5(10)	C(71)-O(11)-C(76)	121.9(8)
C(33)-O(3)-C(35)	123.1(12)	C(33)-O(5)-C(38)	125.2(19)				
Pt(1)-N(1)-C(1)	125.8(4)	Pt(1)-N(2)-C(10)	123.4(6)				
Pt(1)-N(1)-C(5)	116.3(4)	Pt(1)-N(2)-C(6)	115.4(6)				
C(1)-N(1)-C(5)	117.9(5)	C(6)-N(2)-C(10)	121.2(8)				
Pt(1)-N(2)-C(6)	116.9(4)	Pt(1)-N(1)-C(5)	114.1(6)	Pt(2)-N(3)-C(39)	115.6(9)	Pt(3)-N(4)-C(58)	116.2(5)
Pt(1)-N(2)-C(10)	126.2(4)	Pt(1)-N(1)-C(1)	126.1(6)	Pt(2)-N(3)-C(43)	124.9(7)	Pt(3)-N(4)-C(62)	124.6(5)
C(6)-N(2)-C(10)	116.8(6)	C(1)-N(1)-C(5)	119.8(7)	C(39)-N(3)-C(43)	119.5(10)	C(58)-N(4)-C(62)	119.1(7)
N(1)-C(1)-C(2)	122.6(6)	N(2)-C(10)-C(9)	121.8(9)				
C(1)-C(2)-C(3)	120.2(6)	C(8)-C(9)-C(10)	119.0(9)				
C(2)-C(3)-C(4)	117.1(6)	C(7)-C(8)-C(9)	117.1(9)				
C(2)-C(3)-C(11)	123.0(6)	C(9)-C(8)-C(15)	117.8(9)				
C(4)-C(3)-C(11)	119.9(6)	C(7)-C(8)-C(15)	124.7(10)				
C(3)-C(4)-C(5)	120.3(6)	C(6)-C(7)-C(8)	121.4(9)				
N(1)-C(5)-C(4)	121.9(5)	N(2)-C(6)-C(7)	119.3(8)				
N(1)-C(5)-C(6)	114.2(5)	N(2)-C(6)-C(5)	115.4(7)				
C(4)-C(5)-C(6)	123.7(6)	C(5)-C(6)-C(7)	125.2(8)				
N(2)-C(6)-C(5)	113.7(6)	N(1)-C(5)-C(6)	114.3(8)	N(3)-C(39)-C(39)#1	114.0(9)	N(4)-C(58)-C(58)#2	113.5(7)
N(2)-C(6)-C(7)	122.6(5)	N(1)-C(5)-C(4)	119.1(8)	N(3)-C(39)-C(40)	121.8(12)	N(4)-C(58)-C(59)	122.1(8)
C(5)-C(6)-C(7)	123.6(5)	C(4)-C(5)-C(6)	126.5(8)	C(39)#1-C(39)-C(40)	124.2(11)	C(58)#2-C(58)-C(59)	124.3(8)
C(6)-C(7)-C(8)	121.3(6)	C(3)-C(4)-C(5)	121.6(9)	C(39)-C(40)-C(41)	119.4(11)	C(58)-C(59)-C(60)	120.6(8)
C(7)-C(8)-C(9)	115.9(6)	C(2)-C(3)-C(4)	116.0(9)	C(40)-C(41)-C(42)	116.8(13)	C(59)-C(60)-C(61)	116.0(8)
C(7)-C(8)-C(15)	123.6(6)	C(4)-C(3)-C(11)	122.1(10)	C(40)-C(41)-C(44)	119.3(12)	C(59)-C(60)-C(63)	121.7(7)
C(9)-C(8)-C(15)	120.5(7)	C(2)-C(3)-C(11)	122.0(10)	C(42)-C(41)-C(44)	123.9(16)	C(61)-C(60)-C(63)	122.2(8)
C(8)-C(9)-C(10)	121.4(7)	C(1)-C(2)-C(3)	121.1(9)	C(41)-C(42)-C(43)	120.7(15)	C(60)-C(61)-C(62)	121.9(9)
N(2)-C(10)-C(9)	122.1(7)	N(1)-C(1)-C(2)	122.4(9)	N(3)-C(43)-C(42)	121.9(11)	N(4)-C(62)-C(61)	120.3(8)
C(3)-C(11)-C(12)	109.6(7)	C(8)-C(15)-C(16)	108.1(9)				
C(3)-C(11)-C(13)	107.7(6)	C(8)-C(15)-C(17)	106.2(9)				
C(3)-C(11)-C(14)	111.7(6)	C(8)-C(15)-C(18)	110.8(10)				
C(12)-C(11)-C(13)	112.1(8)	C(16)-C(15)-C(17)	109.2(10)				
C(12)-C(11)-C(14)	107.0(7)	C(16)-C(15)-C(18)	110.9(11)				
C(13)-C(11)-C(14)	108.8(7)	C(17)-C(15)-C(18)	111.6(11)				
C(8)-C(15)-C(16)	108.5(8)	C(3)-C(11)-C(12)	108.2(10)	C(41)-C(44)-C(45)	110.4(14)	C(60)-C(63)-C(64)	112.5(9)
C(8)-C(15)-C(17)	113.2(7)	C(3)-C(11)-C(14)	113.2(10)	C(41)-C(44)-C(46)	113.0(16)	C(60)-C(63)-C(65)	106.6(10)
C(8)-C(15)-C(18)	112.9(9)	C(3)-C(11)-C(13)	108.2(10)	C(41)-C(44)-C(47)	110.1(12)	C(60)-C(63)-C(66)	113.5(9)
C(16)-C(15)-C(17)	104.3(9)	C(12)-C(11)-C(13)	112.0(12)	C(45)-C(44)-C(46)	108.5(17)	C(64)-C(63)-C(65)	103.2(12)
C(16)-C(15)-C(18)	109.0(12)	C(12)-C(11)-C(14)	109.9(11)	C(45)-C(44)-C(47)	105.4(17)	C(64)-C(63)-C(66)	112.0(11)

Table S2 continued.

1		2		2'		2''	
C(17)-C(15)-C(18)	108.6(8)	C(13)-C(11)-C(14)	105.4(12)	C(46)-C(44)-C(47)	109.2(14)	C(65)-C(63)-C(66)	108.3(11)
S(1)-C(19)-C(20)	118.3(5)	O(1)-C(19)-C(20)	124.0(8)	O(7)-C(48)-C(49)	125.7(9)	O(10)-C(67)-C(68)	124.1(8)
S(1)-C(19)-C(24)	124.3(5)	O(1)-C(19)-C(24)	119.4(8)	O(7)-C(48)-C(53)	116.0(9)	O(10)-C(67)-C(72)	117.6(8)
C(20)-C(19)-C(24)	117.4(6)	C(20)-C(19)-C(24)	116.7(8)	C(49)-C(48)-C(53)	118.0(9)	C(68)-C(67)-C(72)	118.2(8)
C(19)-C(20)-C(21)	121.5(6)	C(19)-C(20)-C(21)	121.7(9)	C(48)-C(49)-C(50)	121.2(10)	C(67)-C(68)-C(69)	120.7(9)
C(20)-C(21)-C(22)	121.3(6)	C(20)-C(21)-C(22)	122.5(9)	C(49)-C(50)-C(51)	121.7(11)	C(68)-C(69)-C(70)	121.6(9)
C(21)-C(22)-C(23)	116.7(6)	C(21)-C(22)-C(23)	114.6(9)	C(50)-C(51)-C(52)	116.2(10)	C(69)-C(70)-C(71)	117.0(9)
C(21)-C(22)-C(27)	124.5(6)	C(21)-C(22)-C(25)	126.7(9)	C(50)-C(51)-C(54)	126.6(11)	C(69)-C(70)-C(73)	124.6(10)
C(23)-C(22)-C(27)	118.9(6)	C(23)-C(22)-C(25)	118.7(9)	C(52)-C(51)-C(54)	117.0(11)	C(71)-C(70)-C(73)	118.4(9)
O(1)-C(23)-C(22)	122.0(5)	O(2)-C(23)-C(22)	120.9(8)	O(8)-C(52)-C(51)	122.8(9)	O(11)-C(71)-C(70)	121.3(8)
O(1)-C(23)-C(24)	114.9(5)	O(2)-C(23)-C(24)	114.5(8)	O(8)-C(52)-C(53)	114.8(10)	O(11)-C(71)-C(72)	115.4(8)
C(22)-C(23)-C(24)	123.1(6)	C(22)-C(23)-C(24)	124.6(9)	C(51)-C(52)-C(53)	122.5(10)	C(70)-C(71)-C(72)	123.3(8)
C(19)-C(24)-C(23)	120.0(6)	C(19)-C(24)-C(23)	119.9(9)	C(48)-C(53)-C(52)	120.2(11)	C(67)-C(72)-C(71)	119.3(8)
O(1)-C(25)-O(2)	115.8(6)	O(2)-C(28)-O(3)	114.9(14)	O(8)-C(57)-O(9)	114.9(13)	O(11)-C(76)-O(12)	116.4(11)
O(1)-C(25)-C(26)	116.4(6)	O(2)-C(28)-C(27)	117.6(11)	O(8)-C(57)-C(56)	118.1(11)	O(11)-C(76)-C(75)	114.8(11)
O(2)-C(25)-C(26)	127.7(7)	O(3)-C(28)-C(27)	127.4(14)	O(9)-C(57)-C(56)	127.0(12)	O(12)-C(76)-C(75)	128.7(12)
C(25)-C(26)-C(27)	123.6(7)	C(25)-C(27)-C(28)	123.6(12)	C(54)-C(56)-C(57)	122.1(12)	C(73)-C(75)-C(76)	125.7(12)
C(22)-C(27)-C(26)	118.1(6)	C(22)-C(25)-C(27)	119.0(11)	C(51)-C(54)-C(56)	120.4(13)	C(70)-C(73)-C(75)	117.9(11)
C(22)-C(27)-C(28)	121.0(6)	C(22)-C(25)-C(26)	118.5(10)	C(51)-C(54)-C(55)	118.5(11)	C(70)-C(73)-C(74)	120.0(11)
C(26)-C(27)-C(28)	120.9(6)	C(26)-C(25)-C(27)	122.4(11)	C(55)-C(54)-C(56)	121.2(12)	C(74)-C(73)-C(75)	122.1(12)
S(2)-C(29)-C(30)	120.8(4)	O(4)-C(29)-C(30)	124.3(11)				
S(2)-C(29)-C(34)	119.0(4)	O(4)-C(29)-C(34)	113.0(13)				
C(30)-C(29)-C(34)	119.98	C(30)-C(29)-C(34)	122.8(15)				
C(29)-C(30)-C(31)	120.05	C(29)-C(30)-C(31)	119.2(14)				
C(30)-C(31)-C(32)	119.92	C(30)-C(31)-C(32)	121.5(15)				
C(31)-C(32)-C(33)	120.03	C(31)-C(32)-C(33)	116.4(18)				
C(31)-C(32)-C(37)	126.0(8)	C(31)-C(32)-C(35)	119.8(19)				
C(33)-C(32)-C(37)	114.0(8)	C(33)-C(32)-C(35)	124(2)				
O(3)-C(33)-C(32)	122.5(7)	O(5)-C(33)-C(32)	118(2)				
O(3)-C(33)-C(34)	117.4(7)	O(5)-C(33)-C(34)	117.5(19)				
C(32)-C(33)-C(34)	120.00	C(32)-C(33)-C(34)	125.0(17)				
C(29)-C(34)-C(33)	120.02	C(29)-C(34)-C(33)	115.1(16)				
O(3)-C(35)-O(4)	120.8(19)	O(5)-C(38)-O(6)	118(2)				
O(3)-C(35)-C(36)	115.1(12)	O(5)-C(38)-C(37)	113.0(19)				
O(4)-C(35)-C(36)	124.1(16)	O(6)-C(38)-C(37)	129(3)				
C(35)-C(36)-C(37)	123.7(13)	C(35)-C(37)-C(38)	129(2)				
C(32)-C(37)-C(36)	121.3(13)	C(32)-C(35)-C(37)	112(2)				
C(32)-C(37)-C(38)	116.6(12)	C(32)-C(35)-C(36)	123(2)				
C(36)-C(37)-C(38)	122.1(14)	C(36)-C(35)-C(37)	125(2)				

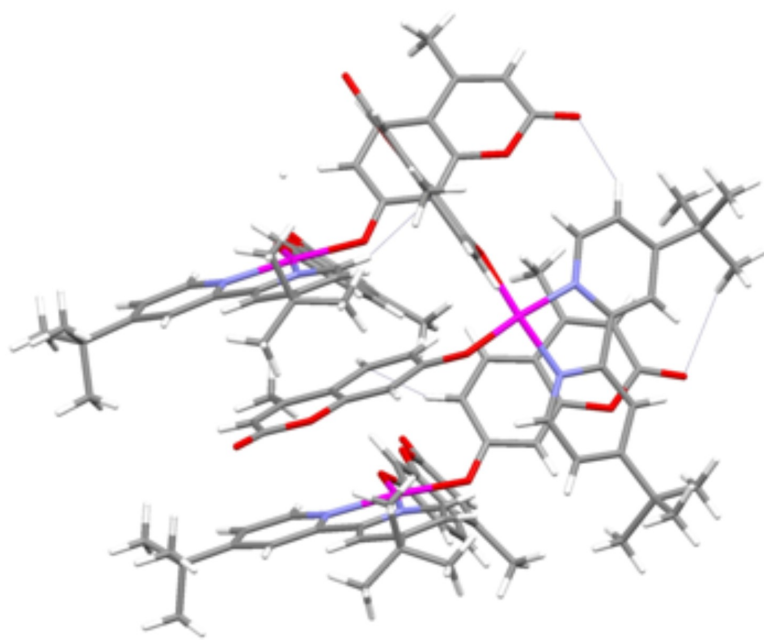


Fig. S1 The three independent molecules within the unit cell of **2**. Hydrogen bonds between individual molecules are indicated by thin lines.

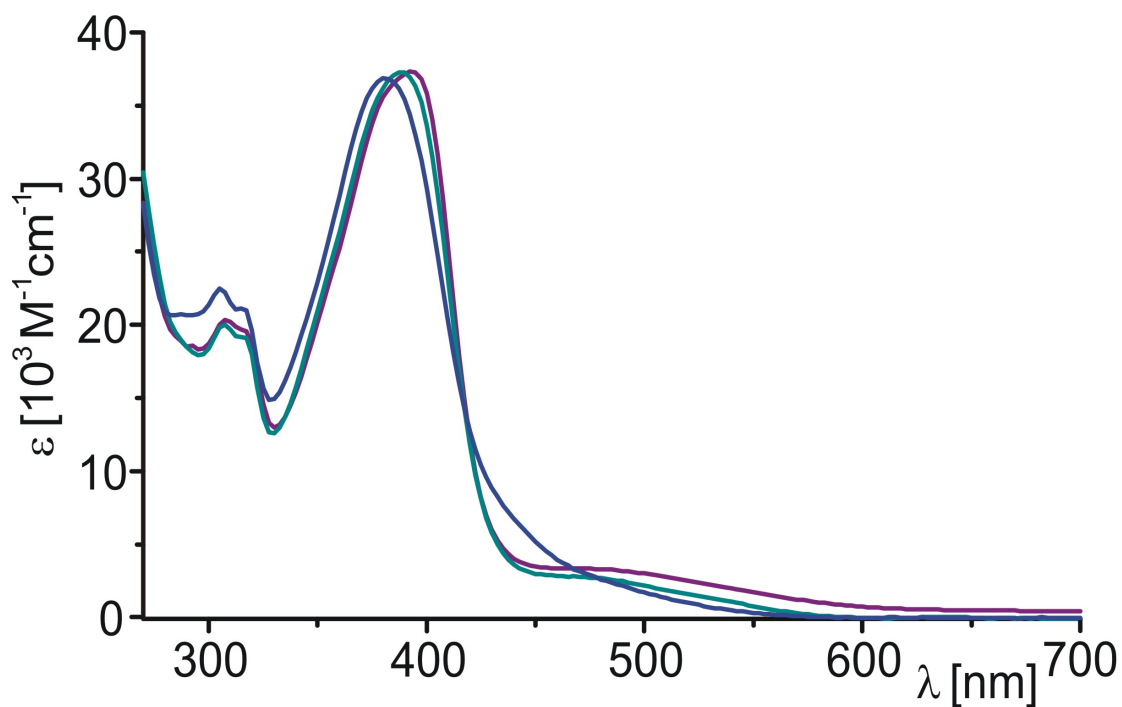


Fig. S2 Absorption spectra of **1** in MeCN (blue), CH₂Cl₂ (cyan) and THF (purple).

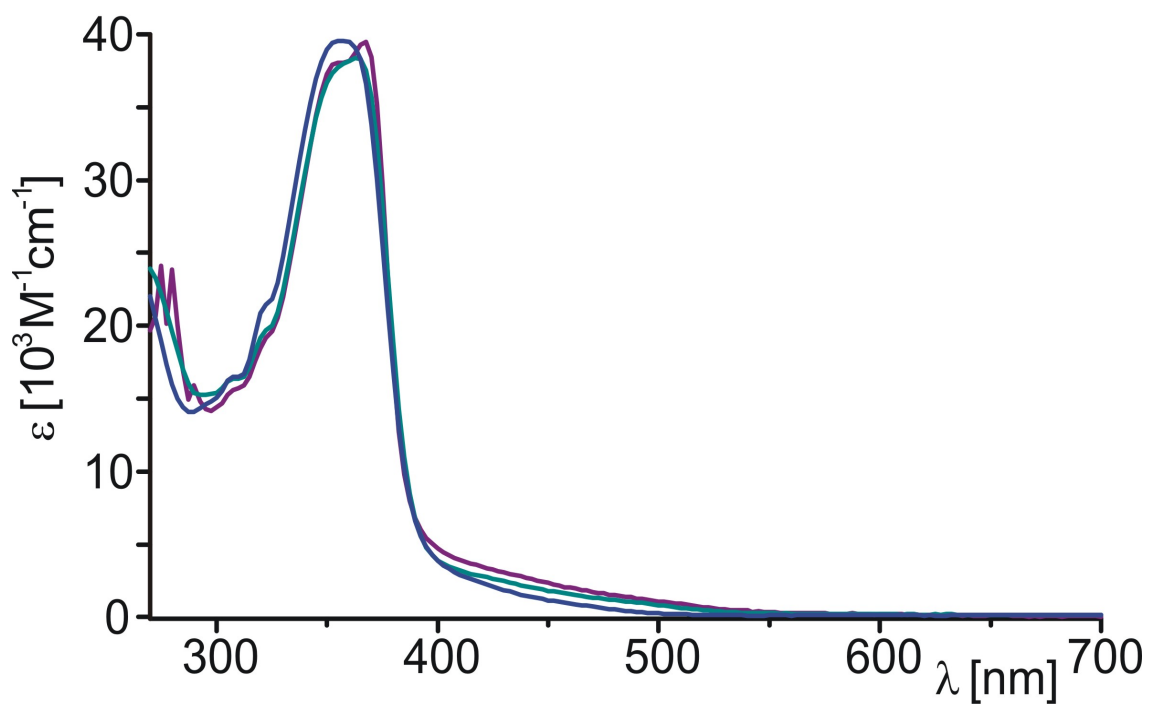


Fig. S3 Absorption spectra of **2** in MeCN (blue), CH₂Cl₂ (cyan) and THF (purple).

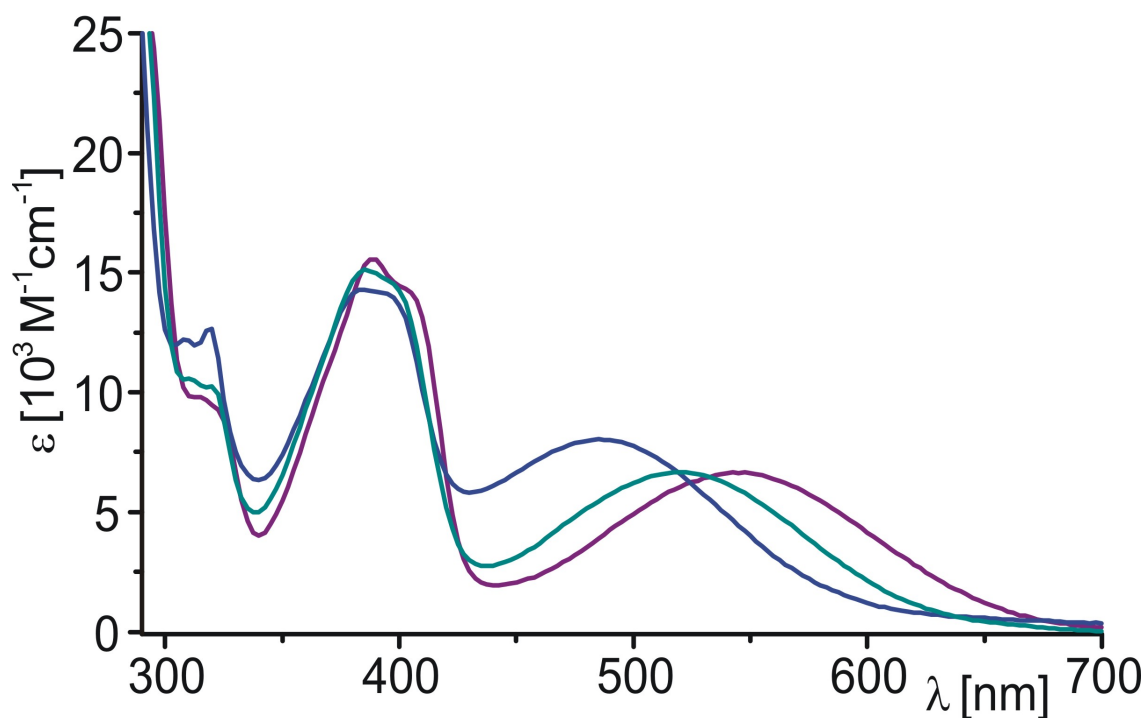


Fig. S4 Absorption spectra of **3** in MeCN (blue), CH₂Cl₂ (cyan) and THF (purple).

Table S3. Absorption data of complexes **1-3** in various solvents

		λ_{\max} ($\epsilon_{\max} / \text{M}^{-1} \text{cm}^{-1}$)
	MeCN	305 (22490), 316 (21190), 381 (36970), 465 (3415)
1	CH ₂ Cl ₂	307 (23540), 317 (22430), 389 (37370), 470 (2810)
	THF	307 (20410), 316 (19560), 393(37300), 487 (3180)
	MeCN	306 (16430), 321 (21090), 356 (39580), 400 (3770)
2	CH ₂ Cl ₂	306 (16430), 322 (22020), 360 (38330), 410 (2810)
	THF	307 (15430), 233 (19170), 355 (38110), 367 (39410), 425 (3250)
	MeCN	308 (12270), 319 (12650), 384 (14320), 394 (14220), 486 (8090)
3	CH ₂ Cl ₂	310 (10530), 320 (10240), 385 (15180), 396 (14650), 522 (6643)
	THF	313 (9820), 322 (9290), 389 (15570), 405 (14280), 547 (6740)

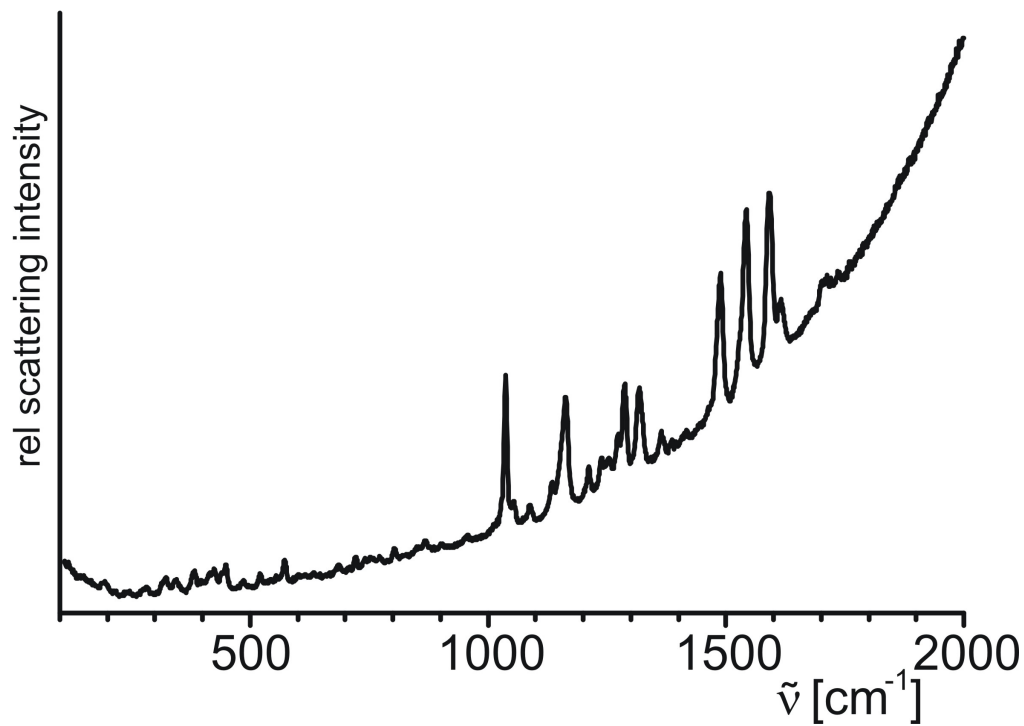


Fig. S5 Resonance Raman spectra of complex 1 (excitation at 488 nm).

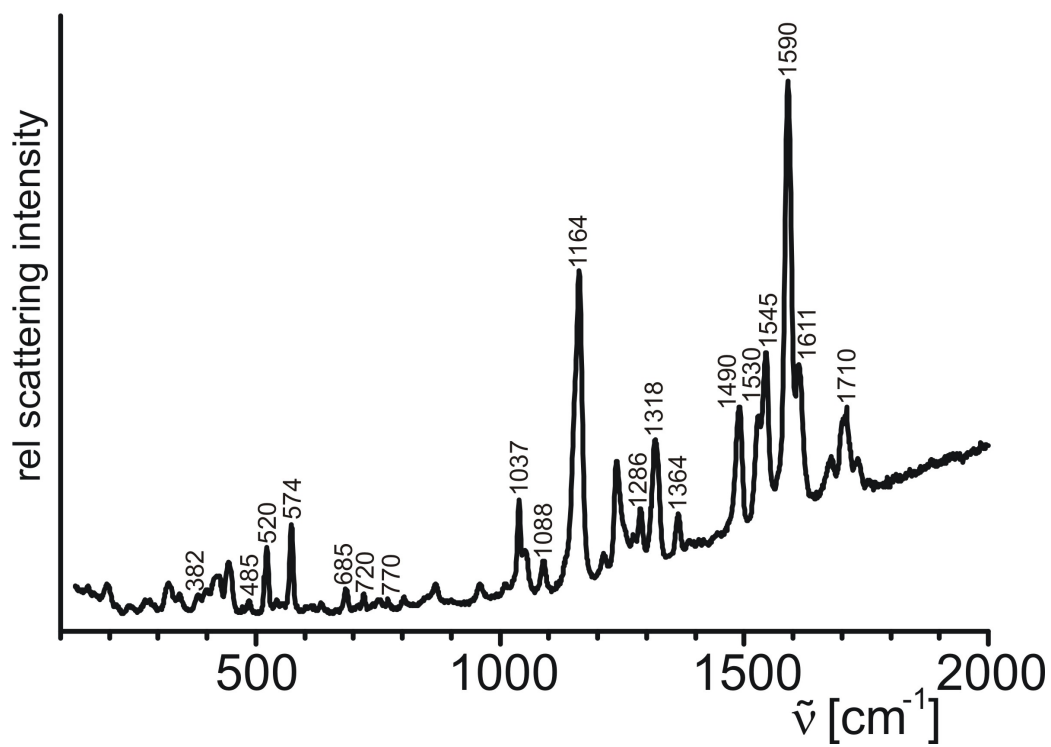


Fig. S6 Resonance Raman spectra of complex 1 (excitation at 454 nm).

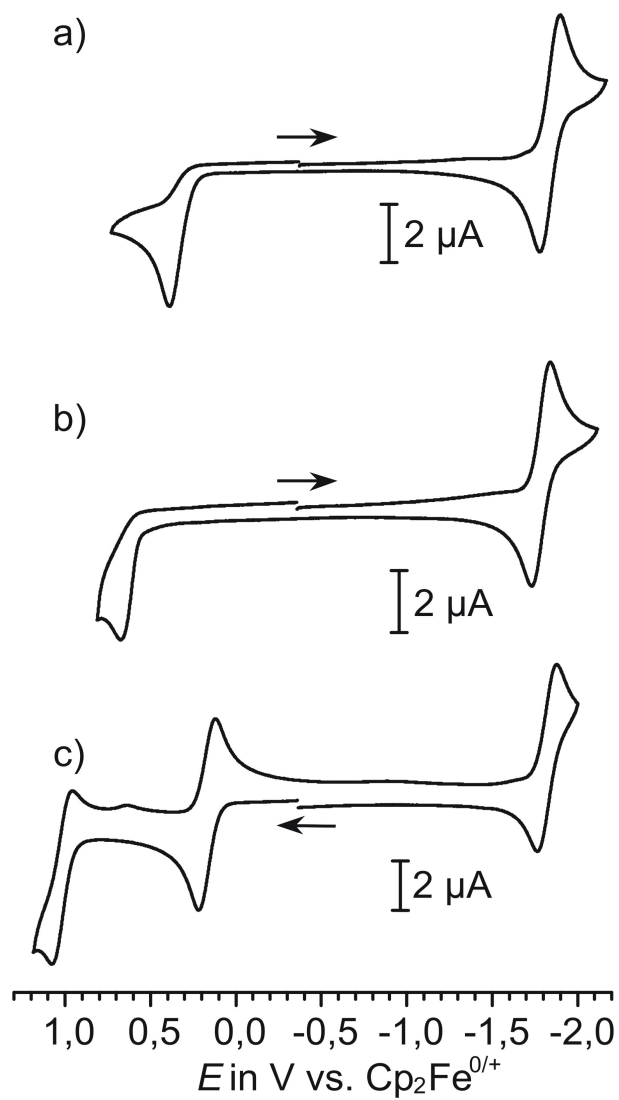


Fig. S7 Cyclic voltammograms of a) **1**, b) **2** and c) **3** in $\text{CH}_2\text{Cl}_2/\text{NBu}_4\text{PF}_6$ (0.1 M) at a sweep rate $\nu = 0.2 \text{ V s}^{-1}$.

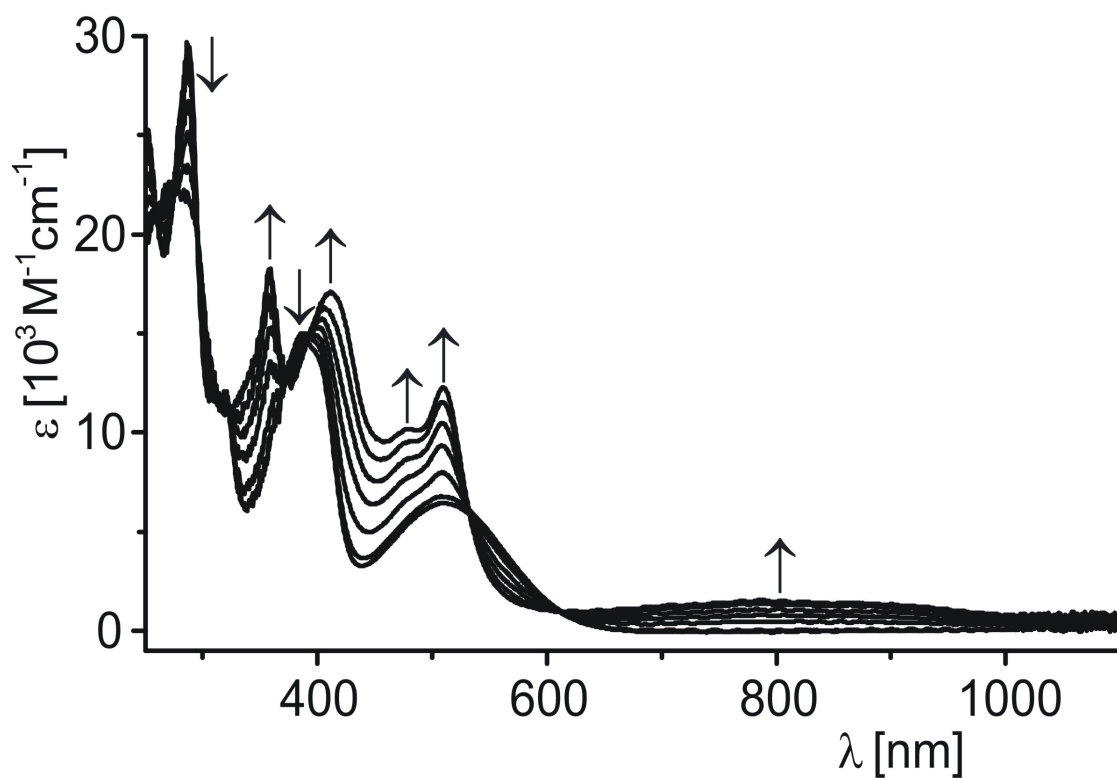


Figure S8 Spectroscopic changes in the UV/Vis/NIR during electrochemical reduction of complex 3 to 3⁻ (DCE/NBu₄PF₆ (0.2 M)) at r.t.

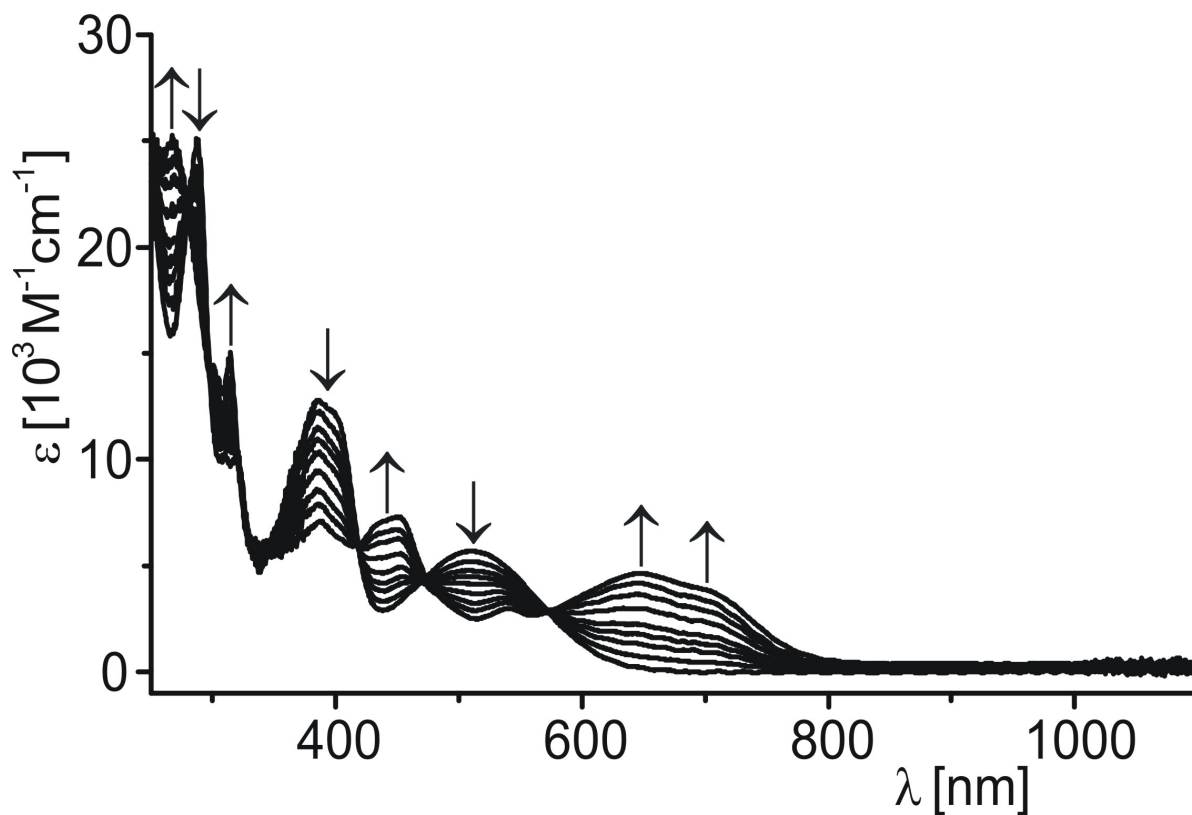


Figure S9 Spectroscopic changes in the UV /Vis /NIR during electrochemical oxidation of complex 3 to 3⁺ (DCE/NBu₄PF₆ (0.2 M)) at r.t.

Table S4. Absorption data for complexes **1-3** in their various oxidation states (1,2-C₂H₄Cl₂, NBu₄PF₆, 0.2 M).

	λ_{\max} (ϵ_{\max} /M ⁻¹ cm ⁻¹)
1	307 (23540), 317 (22430), 389 (37370), 470 (2810)
1^{•-}	264 (35880), 407 (46900), 476 (7780), 504 (7440), 795 (2100)
2	322 (22020), 360 (38330), 410 (2810)
2^{•-}	367 (45160), 469 (5830), 504 (6530), 795 (1770)
3	285 (22470), 385 (15180), 396 (14650), 522 (6643)
3^{•-}	285 (22150), 358 (18350), 410(17170), 478 (10300), 510 (12440), 795 (1680)
3^{•+}	267 (25 090), 315 (14950), 435 (7030), 451 (7330), 539 (2900), 647 (4760), 701 (380)

Table S5. TD-DFT PBE0/PCM-CH₂Cl₂ calculated singlet electronic transitions of complexes **1** and **3** with oscillator strengths larger than 0.005. Transition energies are in eV, corresponding wavelengths (nm) in parentheses, and molar absorptivities in l·mol⁻¹cm⁻¹. Transitions originate from the a¹ ground state. Relevant frontier orbitals are depicted in Figures 4 and S13.

State	Main components (%)	Calculated transitions	Osc. Str.	Expt. Trans. (nm)	Molar abs.
Complex 1					
b	45 (HOMO→LUMO); 55(HOMO-1→LUMO)	2.39 (519)	0.024	470	2810
c	54 (HOMO→LUMO); 44 (HOMO-1→LUMO);	2.42 (513)	0.043		
d	65 (HOMO-1→LUMO+5); 24 (HOMO-1→LUMO+1)	3.21 (387)	0.123	389	37370
e	55 (HOMO→LUMO+1); 20 (HOMO→LUMO+5)	3.35 (370)	0.254		
f	28 (HOMO→LUMO+2); 23 (HOMO→LUMO+3); 21 (HOMO-1→LUMO+2);	3.43 (361)	0.529		
g	79 (HOMO-4→LUMO)	3.47 (357)	0.112		
h	31 (HOMO→LUMO+2); 25 (HOMO-1→LUMO+1); 23 (HOMO-1→LUMO+2)	3.54 (350)	0.061		
i	43 (HOMO-1→LUMO+2); 43 (HOMO-1→LUMO+3)	3.56 (348)	0.084		
j	36 (HOMO-5→LUMO); 35 (HOMO-7→LUMO); 21 (HOMO-6→LUMO)	3.98 (311)	0.105	317	22430
k	50 (HOMO-8→LUMO); 44 (HOMO-9→LUMO)	4.32 (287)	0.245	307	23540
Complex 3					
b	98 (HOMO→LUMO)	2.07 (599)	0.176	522	6643
c	98 (HOMO→LUMO+1)	2.99 (414)	0.023	396	14650
d	96 (HOMO→LUMO+3)	3.31 (375)	0.121	385	15180
e	70 (HOMO-4→LUMO); 21 (HOMO-1→LUMO+3)	3.93 (316)	0.175	320	10240
f	50 (HOMO-1→LUMO+2); 41 (HOMO-1→LUMO+3)	3.98 (311)	0.194	310	10530

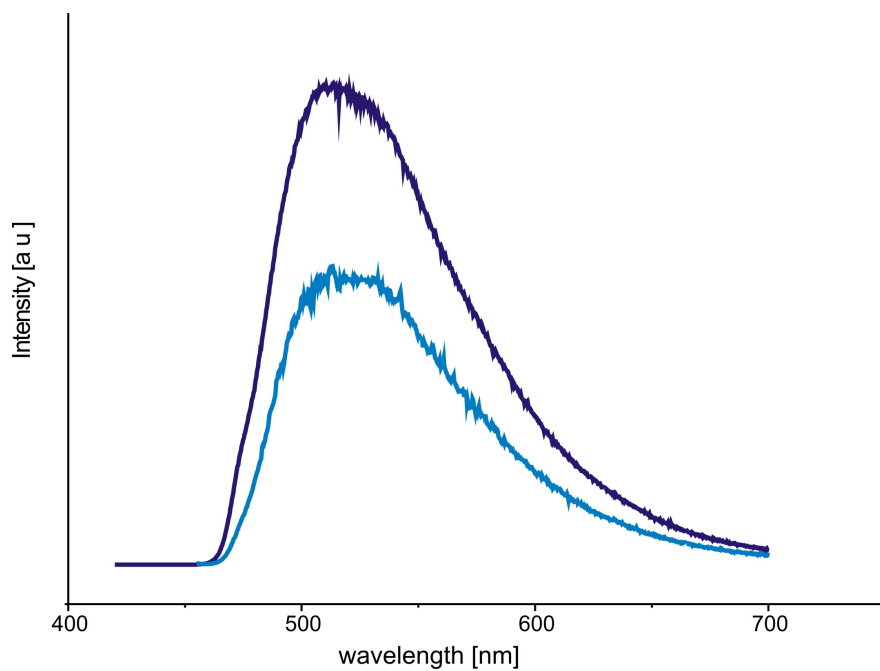


Fig. S10 Emission of complex **2** (CH_2Cl_2 , 77 K) after excitation at 440 nm (cyan) and 370 nm (dark blue).

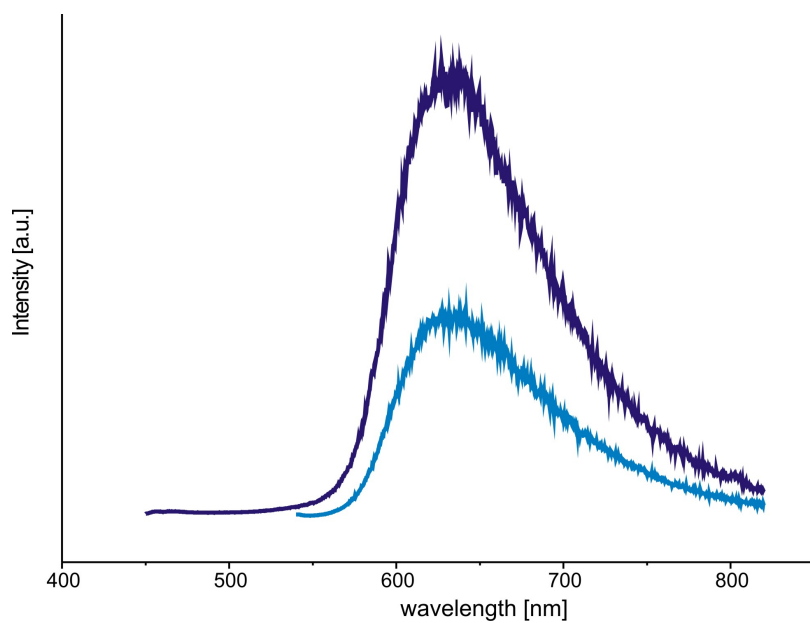


Fig. S11 Emission of complex **3** (CH_2Cl_2 , 77 K) after excitation at 520 nm (cyan) and 400 nm (dark blue).

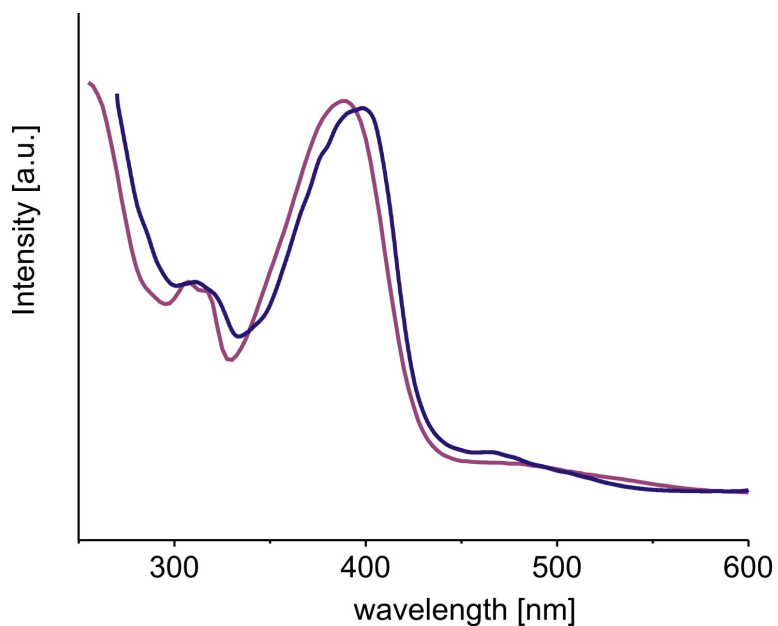


Fig. S12 Excitation (blue, CH_2Cl_2 , 77 K) versus absorption spectrum (purple, CH_2Cl_2 , r. t.) of complex **1**.

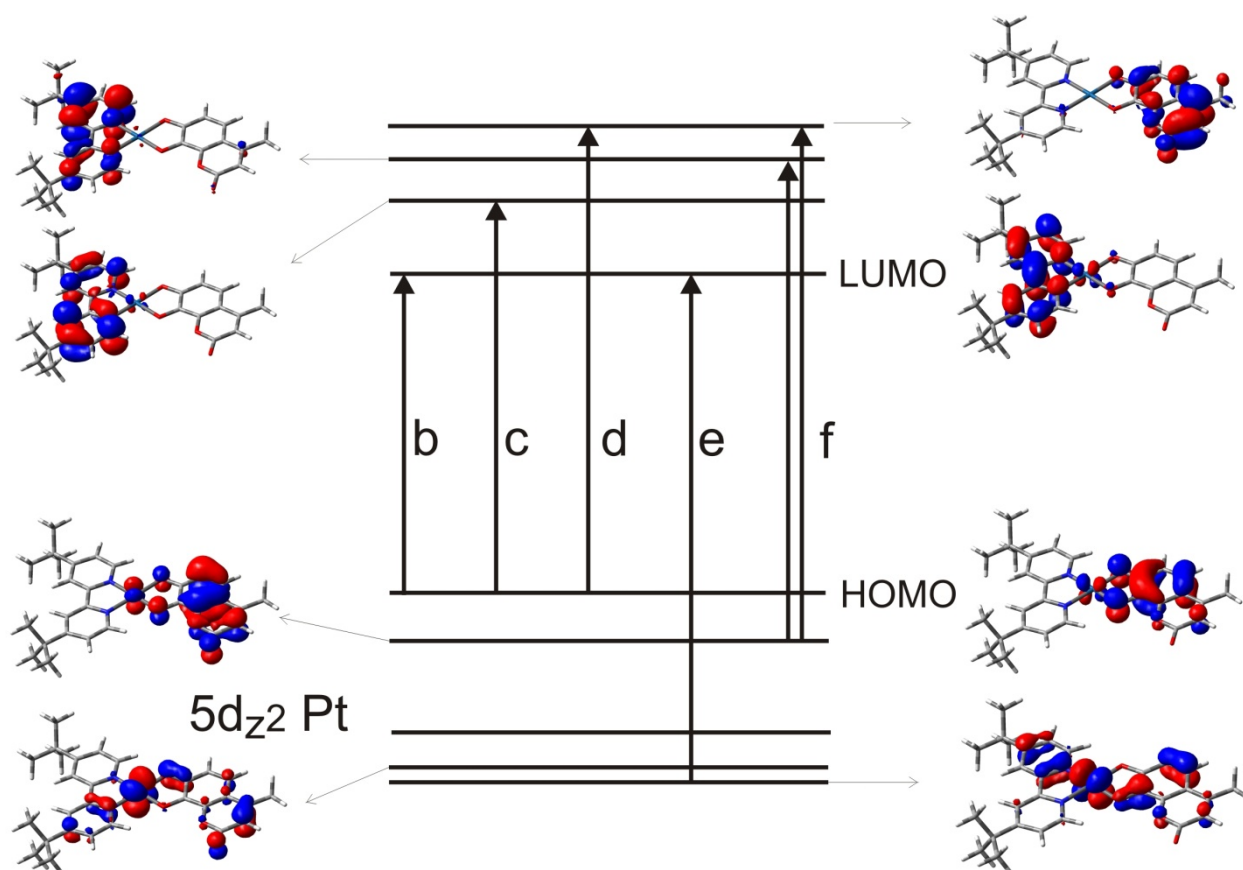


Fig. S13 The qualitative MO scheme of **3**. Arrows indicate the main contributions to the lowest allowed TD DFT calculated transitions.

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