From red to near infra-red OLEDs: the remarkable effect of changing from X = –Cl to –NCS in a cyclometallated [Pt(N^C^N)X] complex {N^C^N = 5-mesityl-1,3-di-(2-pyridyl)benzene}

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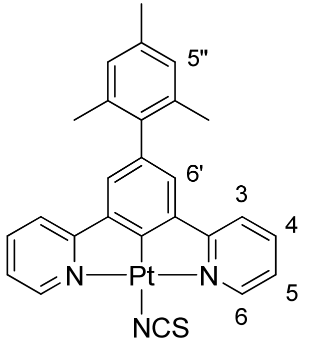
Electronic Supporting Information (ESI)

Synthesis and characterization of [PtL^{6}NCS]

Sodium thiocyanate (14 mg, 0.240 mmol) was added to a suspension of [PtL^{6}Cl] (prepared as previously reported;[1] 70.2 mg, 0.120 mmol) in methanol/acetone (5/20 v/v). The reaction mixture was stirred at room temperature for 1 day and evaporated to dryness. Dichloromethane was added to the crude residue and the solution was filtered. Addition of dry pentane led to the precipitation of a powder which was re-dissolved in CH_2Cl_2 and precipitated with dry pentane. giving the pure product as a red solid (32.5 mg, 45% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (d, J(^{195}Pt) 19 Hz, 2H^6), 7.98 (td, 1H^4), 7.64 (d, 2H^3), 7.33 (td, 2H^5), 7.27 (s, 2H$^{6'}$), 7.02 (s, 2H$^{5''}$), 2.39 (s, 3H *p*-C*H*$_3$), 2.11 (s, 6H *o*-C*H*$_3$).

Numbering system for ^{1}H NMR assignment



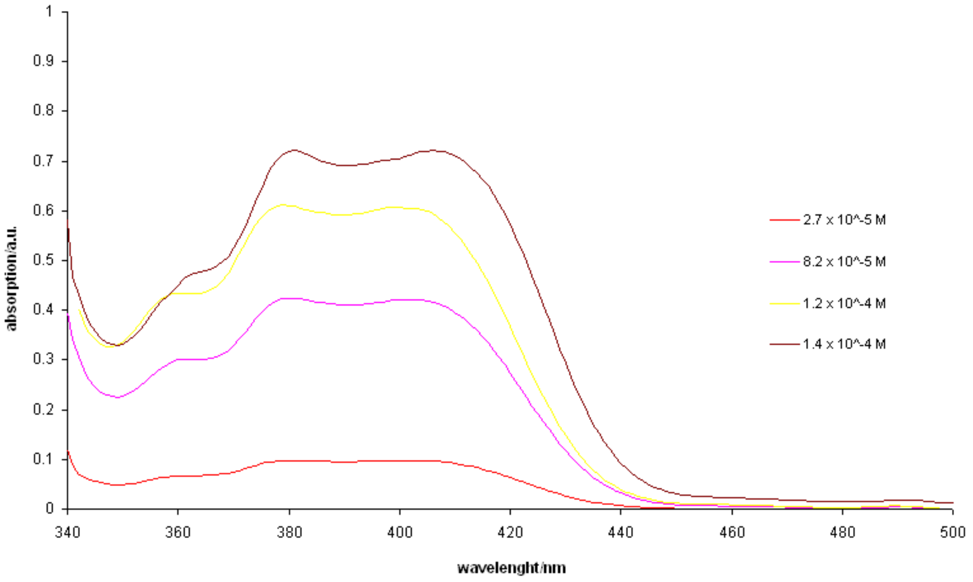
IR ν/cm^{-1} 2097 (SC≡N).

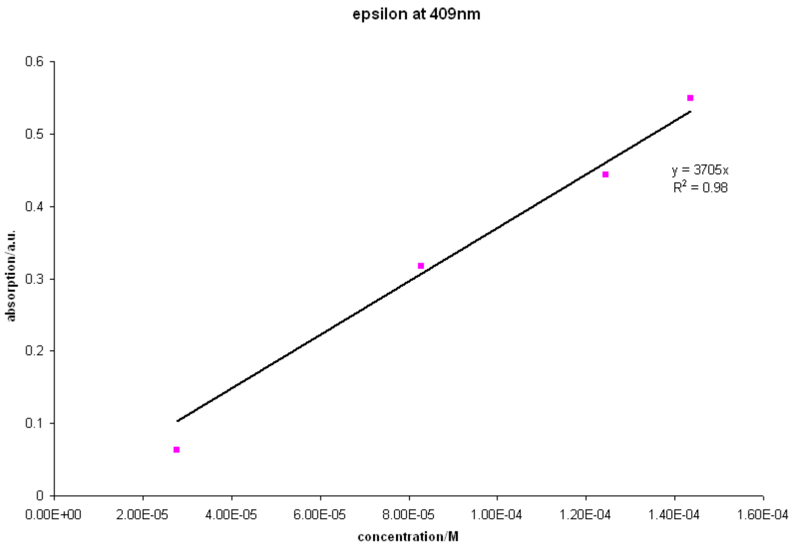
MS FAB+: 440 (M-NCS)$^+$

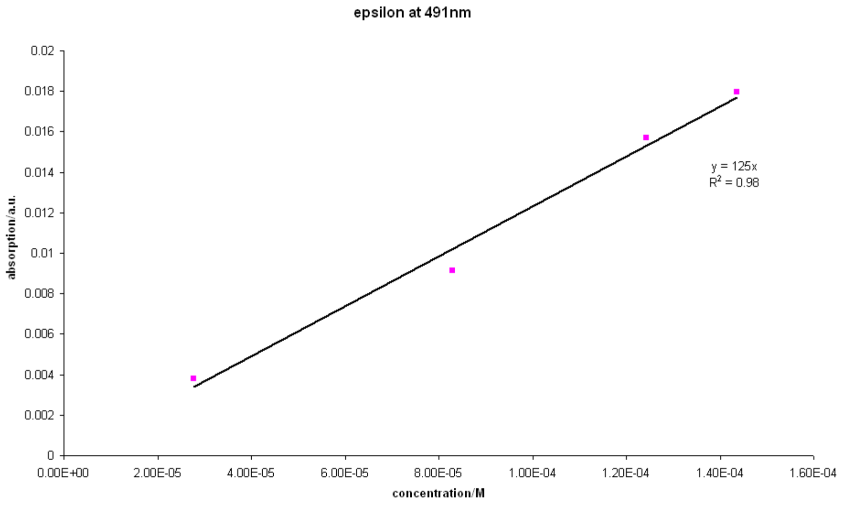
Anal. Calcd for $C_{26}H_{21}N_3PtS$: C, 51.82; H, 3.51; N, 6.97; Found: C, 52.07; H, 3.32; N, 6.72.

1. S. J. Farley, D. L. Rochester, A. L. Thompson, J. A. K. Howard and J. A. G. Williams, *Inorg. Chem.*, 2005, **44**, 9690

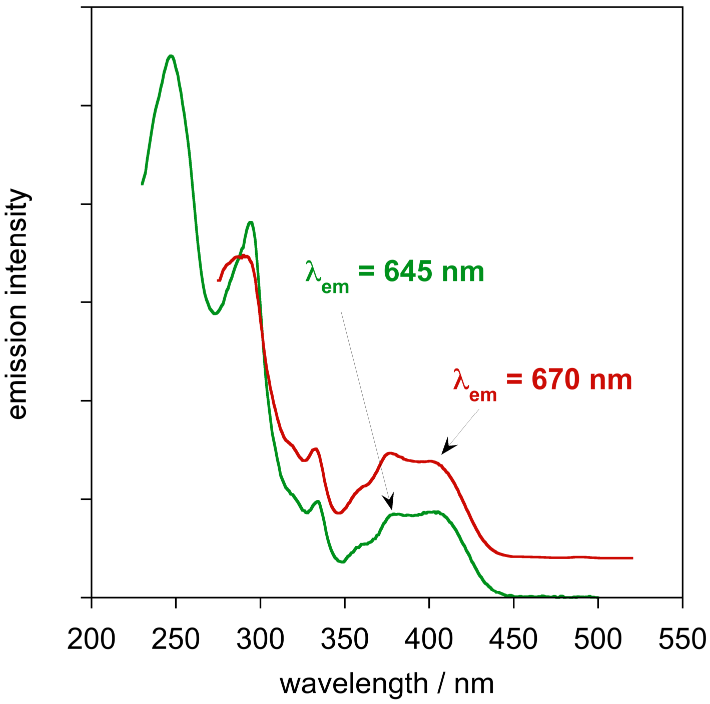
Absorption spectra of [PtL^{6}NCS] in CH_2Cl_2 solution at 298 K over a range of concentrations



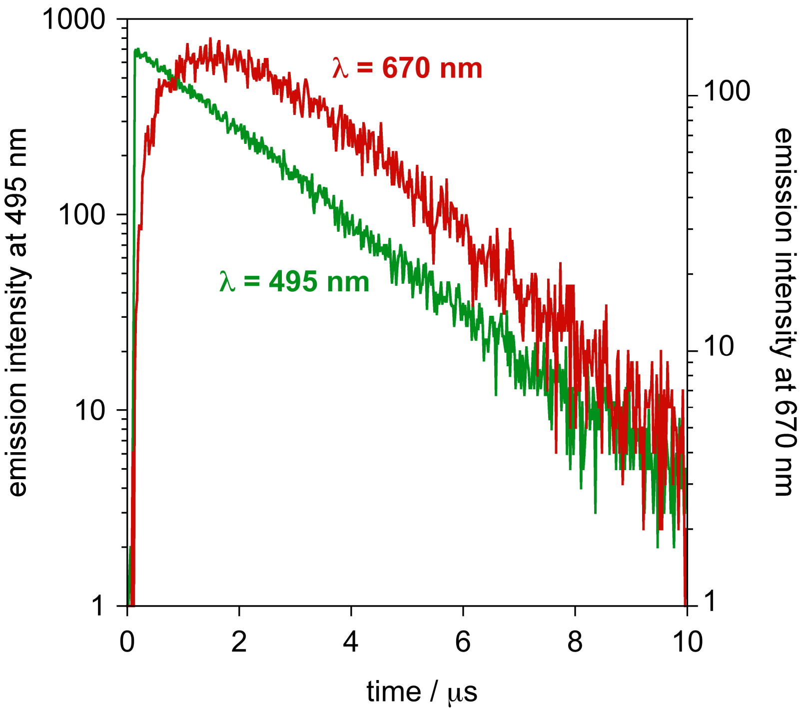




Excitation spectra of the monomer (λ_{em} = 495 nm) and excimer bands (λ_{em} = 670 nm) of [PtL^{6}NCS] in solution in CH_2Cl_2 at 6.7×10^{-4} M. A 1 mm pathlength cell was employed in order to minimise the inner-filter effect in the concentration solution.



The temporal grow-in and decay of the excimer emission for a solution of [PtL^{6}NCS] (CH_2Cl_2, 6.7×10^{-4} M), together with the decay kinetics of the monomer band for the same solution. Measured by TCSPC following excitation at 374 nm with a pulsed diode laser (pulse length ~74 ps, instrument response function FWHM ~1 ns).



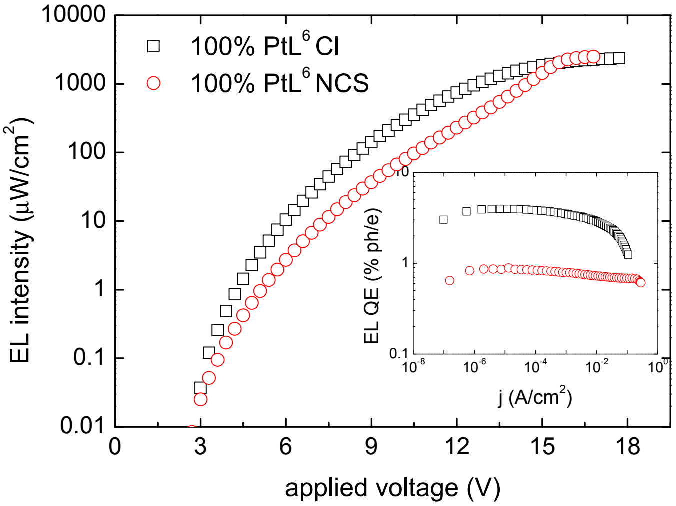
Partial structure determination for [PtL^{6}NCS] and [PtL^{6}Cl]

Structure determinations have been carried out and, although the quality of the obtained data was not sufficient for a full structure publication, all structural features discussed in the paper were established unequivocally from these.

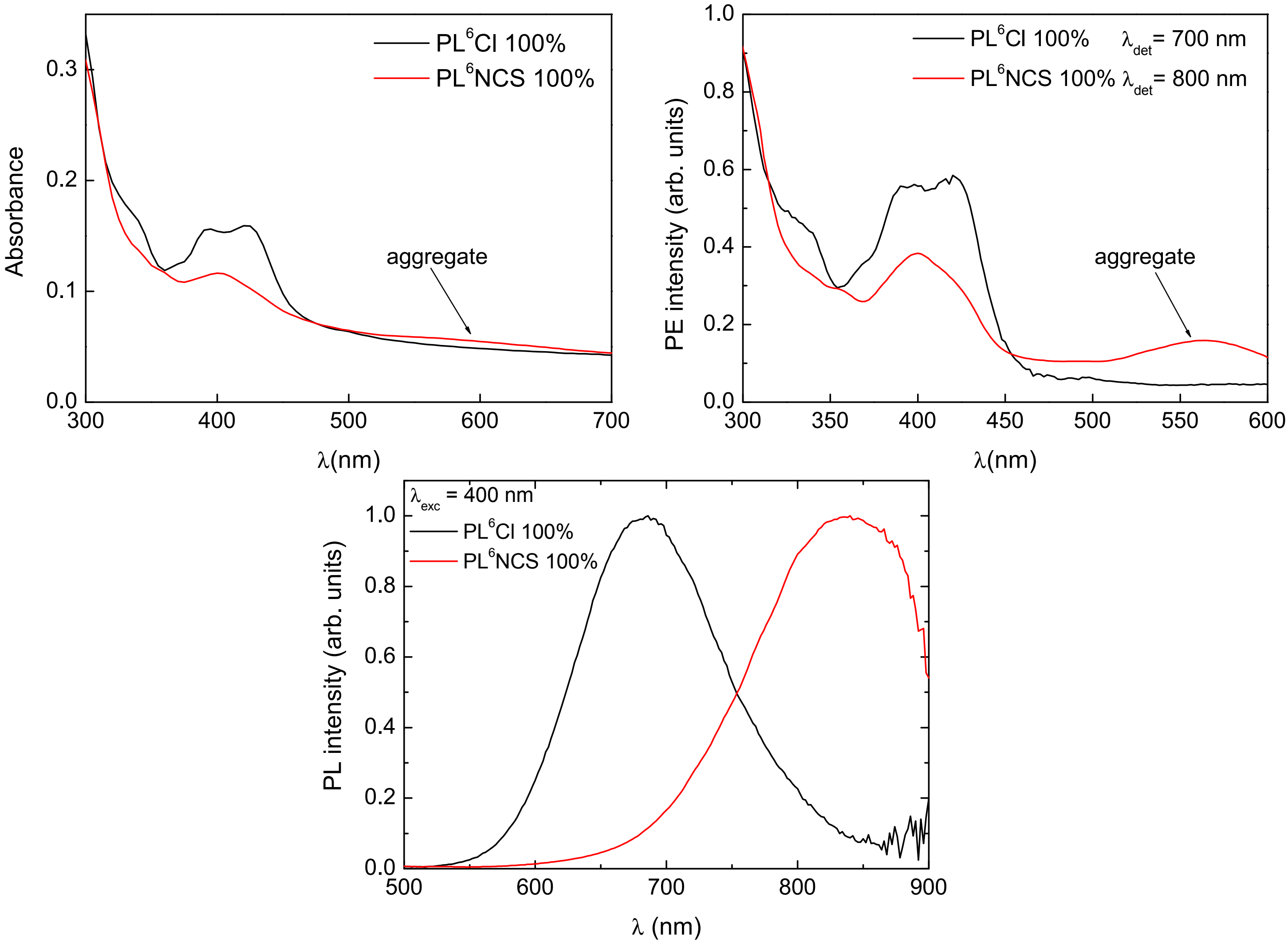
Crystal data for [PtL^{6}NCS]. $C_{26}H_{21}N_3PtS$, M = 602.61, monoclinic, a = 21.786(3), b = 9.735(1), c =22.630(3) Å, β = 93.62(1)°, U = 4790(1) Å^3, T = 293(2) K, space group $P2_{1/n}$ (no. 14), Z = 8, μ = (Mo-Kα) 5.963 mm^{-1}. 11030 reflections (2965 unique; R_{int} = 0.077) were collected at room temperature, employing a 0.10 × 0.04 × 0.03 mm crystal mounted on a Bruker APEX II CCD diffractometer and using graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å). Final $R1$ [$wR2$] values are 0.0445 [0.1389] on 2096 reflections with $I > 2\sigma(I)$ [all data].

Crystal data for [PtL^{6}Cl]. $C_{25}H_{21}N_2PtCl\cdot0.5CH_2Cl_2$, M = 622.44, triclinic, a = 13.0912(6), b = 13.9064(7), c = 15.1284(7) Å, α = 88.36(1), β =66.67(1), γ =67.11(1)°, U = 2461.7(2) Å^3, T = 293(2) K, space group P-1 (no. 2), Z = 4, μ = (Mo-Kα) 5.931 mm^{-1}. 24424 reflections (13827 unique; R_{int} = 0.046) were collected at room temperature, employing a 0.10 × 0.09 × 0.01 mm crystal mounted on a Bruker APEX II CCD diffractometer and using graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å). Final $R1$ [$wR2$] values are 0.0431 [0.1414] on 9206 reflections with $I > 2\sigma(I)$ [all data].

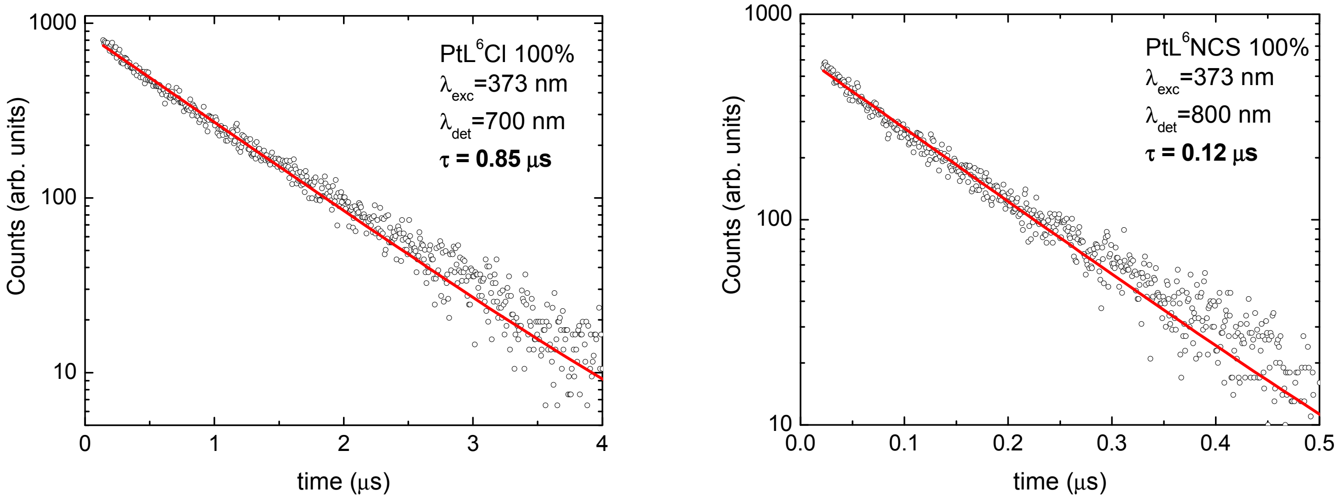
EL intensity towards voltage and EL QE vs j of OLEDs with [PtL^{6}Cl] or [PtL^{6}NCS] neat film as EML



Solid-state photophysics of PtL^{6}Cl and PtL^{6}NCS (50 nm thin film)



Absorbance and photoluminescence (PL) or photo-excitation (PE) spectra were acquired with Perkin- Elmer Lambda 9 UV/VIS/NIR spectrometer and Spex Fluorlog II spectrofluorimeter (spectral response from 200 to 900 nm), respectively.



Single-photon IBH model 5000 counter were employed for the time resolved luminescence measurements.

OLED preparation

OLEDs were fabricated by growing a sequence of thin layers on clean glass substrates pre-coated with a 120 nm-thick layer of indium tin oxide (ITO) with a sheet resistance of 20 Ω per square. A 60 nm thick hole transporting layer of [*N,N'*-diphenyl-*N,N'*-bis (3-methyl)-1,1'-biphenyl-4,4' diamine (TPD)] 75 wt%: [bisphenolpol-A-polycarbonate (MW 32000-36000) (PC)] 25wt% (Aldrich and Polysciences Inc., respectively) blend was spun on top of the ITO from a 10 mg/mL dichloromethane solution at room temperature. All remaining organic layers were deposited in succession by thermal evaporation under vacuum of ~ 10^{-6} hPa, followed by high vacuum (~ 10^{-6} hPa) thermal-evaporation of the cathode layer consisting of 0.5 nm-thick LiF and by a 100 nm-thick Al cap. The emitting layer (EML) was evaporated by co-deposition of the Pt complex and 4,4',4''-tris(*N*-carbazolyl-triphenylamine (TCTA) to form a 30 nm-thick blend film (5 wt% Pt complex : 95 wt% TCTA) or by single deposition of Pt complex to form a 30 nm neat film. The performance of the emissive layer has been optimized by locating the EML between exciton blocking layers of TCTA (10 nm) and 3-phenyl-4-(1'-naphthyl)-5-phenyl-1,2,4-triazole (TAZ), the latter acting also as an electron transporting and hole-blocking layer (30 nm). The current-voltage characteristics were measured with a Keithley Source-Measure unit, model 236, under continuous operation mode, while the light output power was measured with an EG&G power meter and electroluminescence (EL) spectra by StellarNet spectroradiometer. All measurements were carried out at room temperature under argon atmosphere and were reproduced for many runs, excluding any irreversible chemical and morphological changes in the devices.