

## Probing early picosecond dynamics in transition metal complexes using PIRATE

**M. T. Pryce, N. Boyle, A. Coleman and C. Long**  
School of Chemical Sciences, Dublin City University,  
Dublin 9, Ireland

**W. R. Browne and B. L. Feringa**  
Stratingh Institute, OMAC, University Groningen,  
The Netherlands

**K. L. Ronayne and M. Towrie**  
Central Laser Facility, STFC, Rutherford Appleton Laboratory,  
Chilton, Didcot, Oxon., OX11 0QX, UK

Main contact email address

mary.pryce@dcu.ie

Porphyrins play a central role in the design of functional models for biologically important systems such as photosystem II and related electron and energy transfer arrays. The application of porphyrins as components of light harvesting systems has grown considerably in recent years. The versatility in regard to structural modification of porphyrins through the wide range of synthetic strategies available has led to exceptional opportunities for the development of a range of novel molecular devices and molecular based materials, not least in light harvesting, liquid crystals and non linear optical properties.

Metal carbonyl units linked to the porphyrin chromophore act as excellent reporter groups for infrared vibrational spectroscopy, owing to the high molar extinction coefficients of the carbonyl bands in the IR spectrum. Picosecond time resolved infrared spectroscopic studies of metal carbonyl complexes have demonstrated the power of this technique in elucidating photophysical and photochemical reaction pathways. In essence the metal carbonyl linked to the porphyrin macrocycles can act as a probe of transient changes in the electron distribution in donor-acceptor systems. The ability of porphyrins to absorb photons and transfer either electrons or energy to the reaction centre forms the basis of this study, involving picosecond time-resolved infrared spectroscopic (PIRATE) studies. The triplet state of these complexes has previously been investigated in our laboratories, using laser flash photolysis with UV-vis detection. In this study we probed the changes in the metal carbonyl region following excitation with either 400 or 532 nm. Both the free base mono pyridyl triphenyl porphyrin pentacarbonyl complexes (MPyTPPCr(CO)<sub>5</sub> and MPyTPPW(CO)<sub>5</sub>) and the zinc metallated porphyrin complexes (ZnMPyTPPCr(CO)<sub>5</sub> and ZnMPyTPPW(CO)<sub>5</sub>) (Figure 1) were studied.

In addition a number of acetylene cobalt carbonyl compounds were studied. Such systems are directly relevant to the Pauson-Khand reaction. Also, the isomerisation process in (η<sup>6</sup>-stilbene)Cr(CO)<sub>3</sub> was probed.

Excitation of MPyTPPW(CO)<sub>5</sub> at 400 nm in THF, results in formation of negative bands within 2 ps at 2063 and 1929 cm<sup>-1</sup>, which indicates depletion of the parent. In addition positive bands are formed at 2054, 1956, 1910 and 1877 cm<sup>-1</sup>. These bands all decay over ~250 ps and are assigned to a single excited state species because these bands decay with almost complete recovery of the parent absorptions (figure 2).

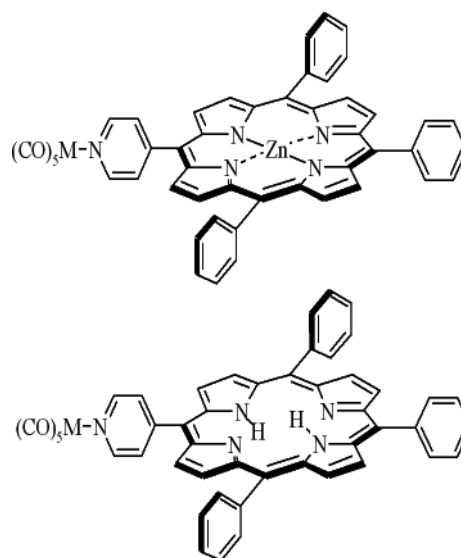


Figure 1

For both MPyTPPW(CO)<sub>5</sub> and ZnMPyTPPW(CO)<sub>5</sub>, the parent bands recover by ~95%. Additional weak features are evident after 250 ps and are assigned to THFW(CO)<sub>5</sub>. The transient spectra following excitation of either MPyTPPCr(CO)<sub>5</sub> or ZnMPyTPPCr(CO)<sub>5</sub> are similar to that previously described for MPyTPPW(CO)<sub>5</sub>. Following excitation of MPyTPPCr(CO)<sub>5</sub> new bands are generated at 2054, 1965, 1919 and 1854 cm<sup>-1</sup> which decay over 100 ps. The parent band at 1933 cm<sup>-1</sup> recovers by approximately 80%, and the bands observed after 50 ps at 2058 and 1877 cm<sup>-1</sup> are assigned to THFCr(CO)<sub>5</sub>. There was very little difference between the free base or zinc metallated porphyrins following excitation at 400 nm. The experiments were performed in a number of solvents, including THF, CH<sub>3</sub>CN, CH<sub>2</sub>Cl<sub>2</sub> and methylcyclohexane.

Excitation of trans-(η<sup>6</sup>-stilbene)Cr(CO)<sub>3</sub> with 400 nm, produced positive bands at 2012, 1961, 1947 and 1891 cm<sup>-1</sup> and negative bands at 1915 and 1890 cm<sup>-1</sup> (the latter two assigned to depletion of the parent). The bands at 1961 and 1891 cm<sup>-1</sup> are assigned to an excited state species which is the precursor to trans-(η<sup>6</sup>-stilbene)Cr(CO)<sub>2</sub>, as the bands at 1961 and 1891 cm<sup>-1</sup> decay over 100 ps with the formation of bands at 1929 and 1873 cm<sup>-1</sup> assigned to trans-(η<sup>6</sup>-stilbene)Cr(CO)<sub>2</sub> (Figure 2). The bands at 1961 and 1891 cm<sup>-1</sup> are assigned to a <sup>1</sup>MLCT excited state. This

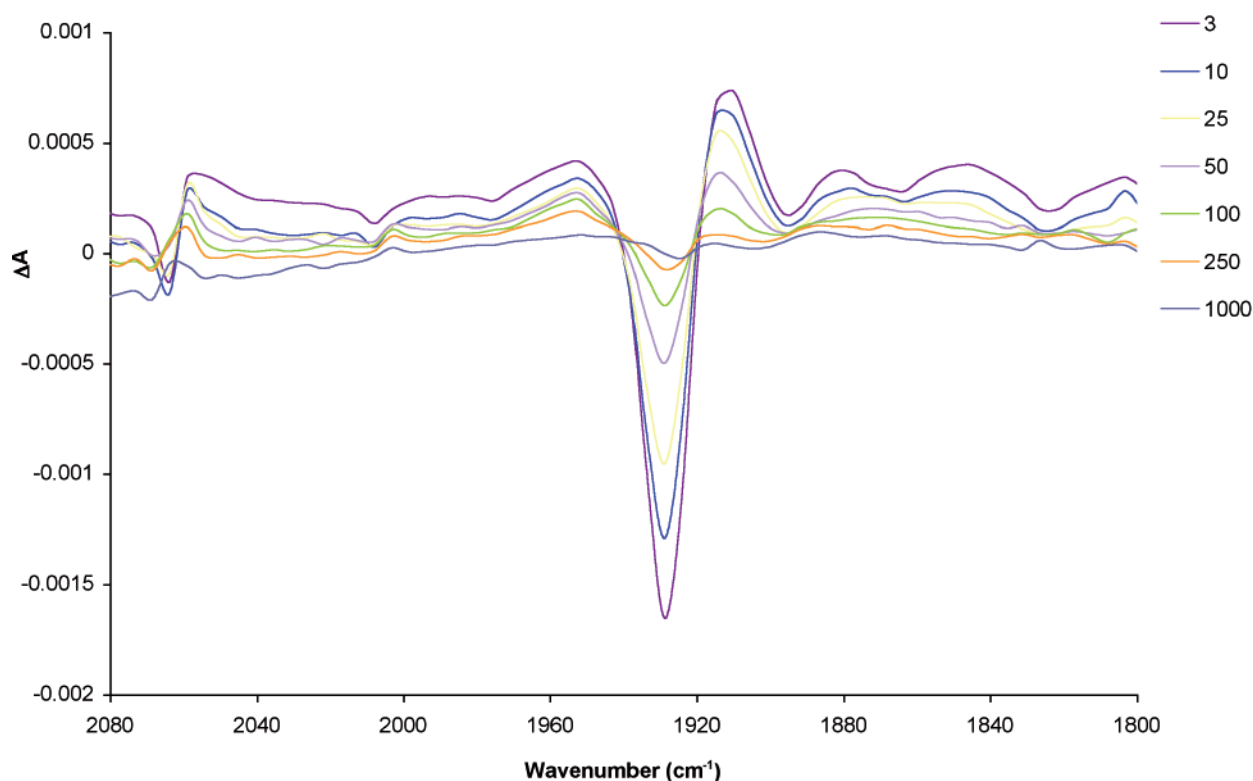


Figure 2. TRIR spectra of MPyTPPW(CO)<sub>5</sub> in THF following excitation at 400 nm.

state produces the CO-loss species over the avoided crossing to the CO-loss state <sup>1</sup>MCCT. The bands at 2012 and 1947 cm<sup>-1</sup> are a second excited state possibly a M(C=C)CT. Similar results were obtained for cis-(η<sup>6</sup>-stilbene)Cr(CO)<sub>3</sub>.

The last aspect of this report deals with the photochemistry of [Co<sub>2</sub>(CO)<sub>6</sub>(μ<sub>2</sub>-alkyne)] complexes. Following excitation of diphenylacetyleneCo<sub>2</sub>(CO)<sub>6</sub> new infrared bands were observed at 2074, 2041 and a further broad band at 1992 cm<sup>-1</sup>, in addition to depletion of the parent bands at 2098, 2052, 2020 cm<sup>-1</sup> (figure 3). A short ~10 ps vibrational cooling component followed by a 70-80 ps recovery with no permanent bleaching was observed for all systems studied. The photochemistry was essentially independent of the solvent employed (pentane, THF, acetonitrile, DCM). The transient species observed here is thought to arise from homolysis of the Co-Co bond which after undergoing vibrational cooling recombines within 80 ps.

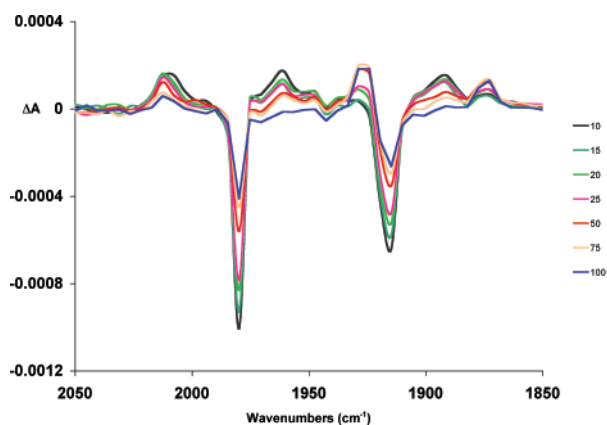


Figure 3. TRIR spectra of trans-(stilbene)Cr(CO)<sub>3</sub> in pentane following excitation at 400 nm.