

Excited-State Relaxation Dynamics of Re(I) Tricarbonyl Complexes with Macrocyclic Phenanthroline Ligands Studied by Time-Resolved IR Spectroscopy

SUPPLEMENTARY INFORMATION

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Characterization of $[\text{Re}(\text{L})(\text{CO})_3(\text{phen-macrocycle})]^n$ complexes

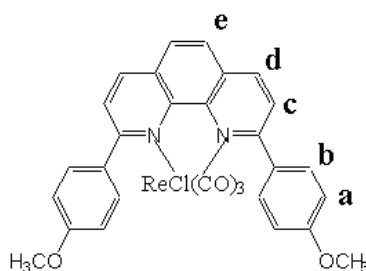
$[\text{Re}(\text{Cl})(\text{CO})_3(\text{dap})]$

77 % yield

$^1\text{H-NMR}$ CDCl_3 270 MHz: 8.51 (2 H, d, J 8.4 Hz, CHd), 8.00 (2 H, s, CHe), 7.89 (2 H, d, J 8.2 Hz, CHc), 7.69 (4 H, d, J 7.7 Hz, CHb), 7.06 (4 H, d, J 8.4 Hz, CHa), 3.88 (2 H, s, CH_3)

FTIR (CH_2Cl_2) $\nu(\text{CO}) = 2022(\text{s}), 1923(\text{b}), 1885(\text{b})$

Mass Spec.(ES) m/z : Calculated for $\text{C}_{29}\text{H}_{20}\text{N}_2\text{O}_5$ $^{187}\text{Re}^+$ (M-Cl): 663.0930. Found: 663.0966



Structure of $[\text{Re}(\text{Cl})(\text{CO})_3(\text{dap})]$. Labels a-d show the NMR assignment.

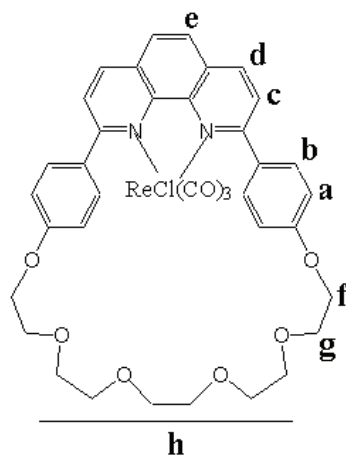
$[\text{Re}(\text{Cl})(\text{CO})_3(\text{m30})]$

80% yield

$^1\text{H-NMR}$ CDCl_3 270 MHz: 8.53 (4 H, d, J 8.4 Hz, CHd), 8.25 (2 H, d, J 8.2 Hz, CHb), 8.07 (2 H, d, J 8.4 Hz, CHc), 7.73 (2 H, s, CHe), 7.18 (4 H, d, J 8.2 Hz, CHa), 4.33 (4 H, t, J 4.7 Hz, CHf), 3.83 (4 H, t, J 4.9 Hz, CHg), 3.71 (12 H, m, CHh)

FTIR (CH_2Cl_2) $\nu(\text{CO}) = 2021(\text{s}), 1924(\text{b}), 1885(\text{b})$

Mass Spec.(ES) m/z : Calculated for $\text{C}_{37}\text{H}_{34}\text{N}_2\text{O}_9$ $^{187}\text{Re}^+$ (M-Cl): 837.1822. Found: 837.1860



Structure of $[\text{ReCl}(\text{CO})_3(\text{m30})]$. Labels a-h show the NMR assignment.

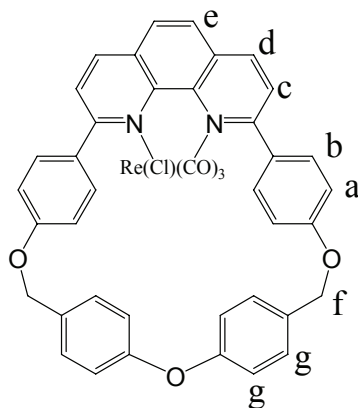
$[\text{Re}(\text{Cl})(\text{CO})_3(\text{m27})]$

82% yield

$^1\text{H-NMR}$ CDCl_3 270 MHz: 8.49 (2 H, d, J 8.4 Hz, CHd), 7.96 (4 H, d, J 8.4 Hz, CHb), 7.50 (2 H, d, J 8.2 Hz, CHe), 7.49 (2 H, d, J 8.4 Hz, CHc), 7.35 (4 H, d, J 8.4 Hz, CHa), 7.15 (4 H, m, CHf), 6.69 (8 H, m, CHg)

FTIR (CH_2Cl_2) $\nu(\text{CO}) = 2023(\text{s}), 1925(\text{b}), 1887(\text{b})$

Mass Spec.(ES) m/z : Calculated for $\text{C}_{41}\text{H}_{26}\text{N}_2\text{O}_6$ $^{187}\text{Re}^+$ (M-Cl): 829.1348. Found: 829.1367



Structure of $[\text{Re}(\text{Cl})(\text{CO})_3(\text{m27})]$. Labels a-g show the NMR assignment.

[Re(Etpy)(CO)₃(dap)]PF₆

FTIR (MeCN) $\nu(\text{CO}) = 2029(\text{s}), 1923(\text{b})$

Mass Spec.(ES) m/z: Calculated for C₃₆H₂₉N₃O₅ ¹⁸⁷Re⁺ (M⁺): 770.1654. Found: 770.1666

[Re(Etpy)(CO)₃(m27)]PF₆

FTIR (MeCN) $\nu(\text{CO}) = 2029(\text{s}), 1924(\text{b})$

Mass Spec.(Low res ES) m/z: Calculated for C₄₈H₃₅N₃O₆ ¹⁸⁷Re (M⁺ + arginine): 1110.3.

Found: 1110.4

[Re(Etpy)(CO)₃(m30)]PF₆

FTIR (MeCN) $\nu(\text{CO}) = 2028(\text{s}), 1921(\text{b})$

Mass Spec.(Low res ES) m/z: Calculated for C₄₄H₄₃N₃O₉ ¹⁸⁷Re (M⁺ + arginine): 1118.4.

Found: 1118.4

FIGURES

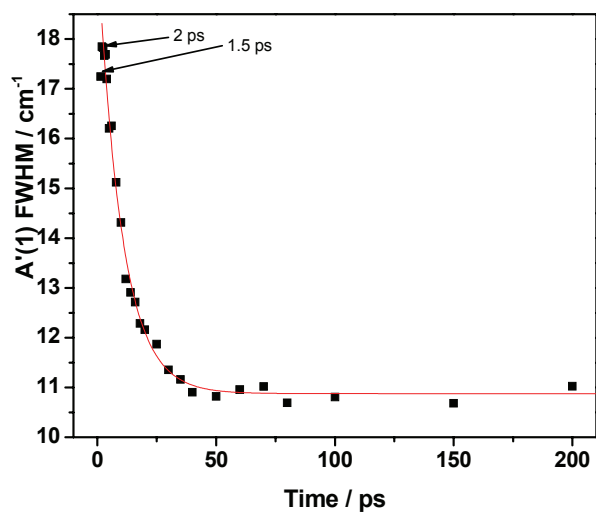


Fig. S1. Time-dependence of the excited-state A'(1) $\nu(\text{CO})$ bandwidth (FWHM) of [Re(Cl)(CO)₃(dap)] in CH₂Cl₂. Time constant 10.1 ± 0.5 ps. Note the band broadening between 1.5 and 2 ps.

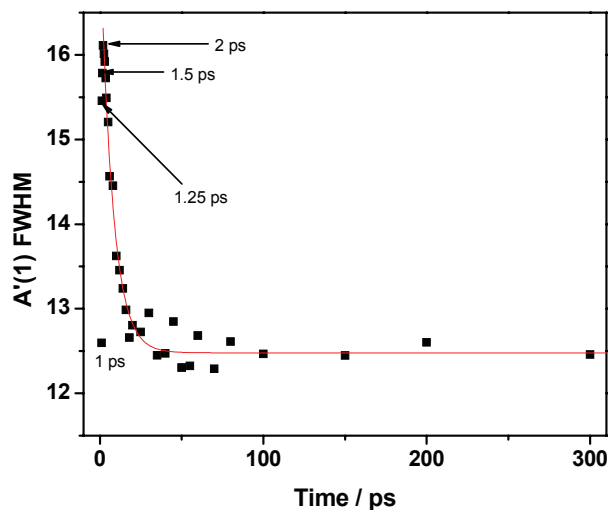


Fig. S2. Time-dependence of the excited-state A'(1) $\nu(\text{CO})$ bandwidth (FWHM) of $[\text{Re}(\text{Cl})(\text{CO})_3(\text{m27})]$ in CH_2Cl_2 . Time constant 7.5 ± 0.5 ps. Note the band broadening between 1 and 2 ps.

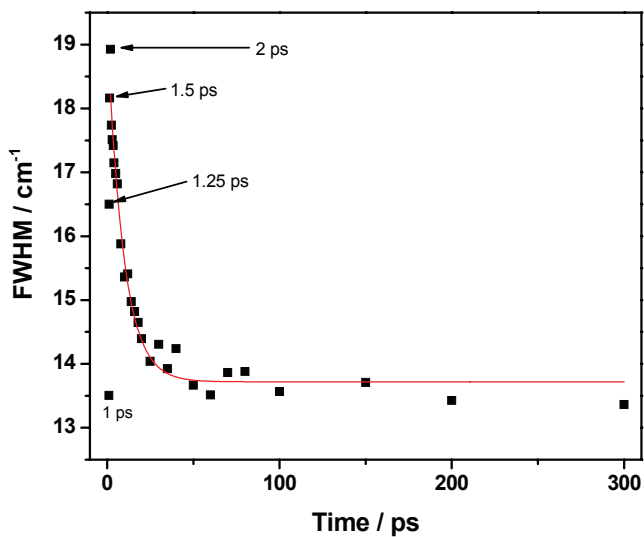


Fig. S3. Time-dependence of the excited-state A'(1) $\nu(\text{CO})$ bandwidth (FWHM) of $[\text{Re}(\text{Cl})(\text{CO})_3(\text{m30})]$ in CH_2Cl_2 . Time constant 9.3 ± 0.8 ps. Note the band broadening between 1 and 2 ps. Fitted curve starts at 2 ps.

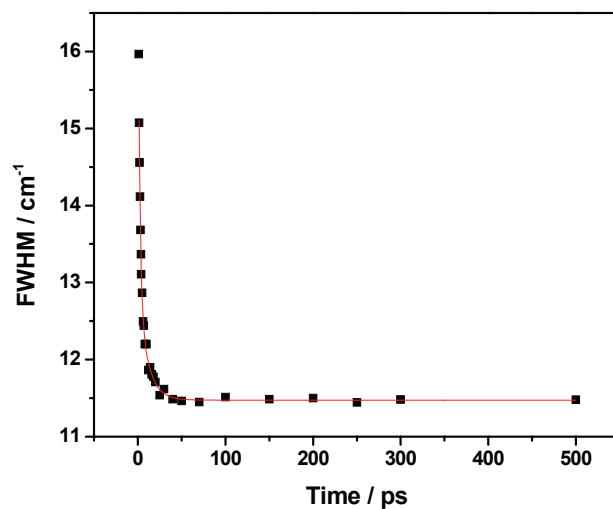


Fig. S4. Time-dependence of the excited-state A'(1) $\nu(\text{CO})$ bandwidth (FWHM) of $[\text{Re}(\text{Cl})(\text{CO})_3(\text{phen})]$ in CH_2Cl_2 . Biexponential narrowing with time constants of 2.0 ± 0.2 and 10.6 ± 1.6 ps. Fitted curve starts at 1.5 ps.