Supplementary Information for **Solvent Effects on the Photophysical Properties of Bu_4N[(4,4′-bpy)$Re(CO)_3$(bpy-5,5'-diCOO)] Complex. A Combined Experimental and Computational Study**

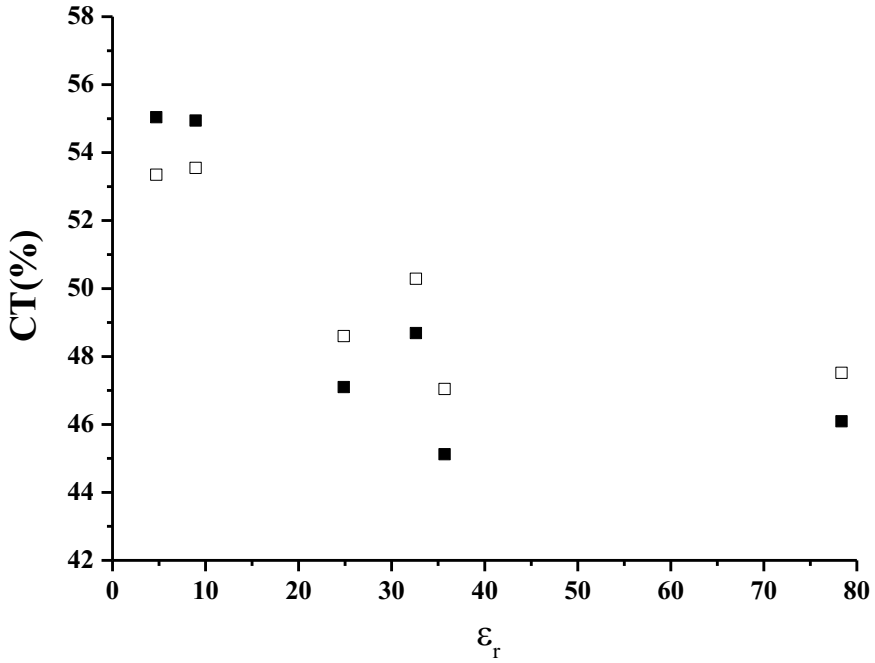

Figure S1. Charge transfer percentage for both $MLLCT_{Re(CO)_3 \rightarrow 4,4'\text{-bpy}}$ (■) and $MLLCT_{Re(CO)_3 \rightarrow \text{bpy-5,5'-diCOO}}$ (□) transitions vs dielectric constant, ε_r.

The calculated electronic spectra of $[(4,4'\text{-bpy})Re(CO)_3(\text{bpy-5,5'-diCOO})]^-$ are simulated from the theoretical results to ease the comparison with experimental data. The calculated spectra are obtained by summing Gaussian functions centered at each calculated wavelength with the maxima related to the value of the oscillator strengths using **eq. 1**

$$\varepsilon(\tilde{\upsilon}) = \frac{2.175\text{x}10^{8}\, Lmol^{-1}cm^{-2}}{\Delta_{½}\tilde{\upsilon}}\left(f_{\text{osc}}\right)\exp\left[-2.772\left(\frac{\tilde{\upsilon}-\tilde{\upsilon}_{i\rightarrow f}}{\Delta_{½}\tilde{\upsilon}}\right)^{2}\right] \qquad \textbf{(1)}$$

This is the formula that GaussSum uses to convolute spectra [1]. In this equation, the parametrical value of the fwhm of the band is given in units of cm^{-1} and is symbolized by Δ½$\tilde{\upsilon}$, f_{osc} is the oscillator strength and $\tilde{\upsilon}_{i\rightarrow f}$ is the frequency (in units of cm^{-1}) corresponding to the wavelength of the calculated electronic transition.

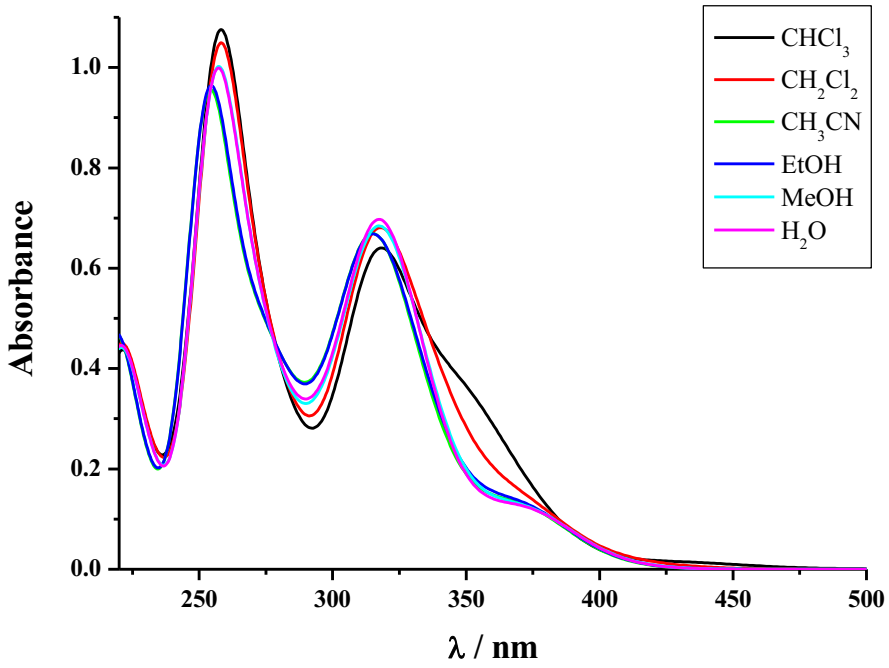

Figure S2. Calculated absorption spectra of [(4,4´-bpy)Re(CO)$_3$(bpy-5,5'-diCOO)]$^-$ at the B3LYP/LanL2DZ level of theory for all the solvents under study.

Lists of outputs files from G09:

B3LYP SP S0@T1.out: Single point calculation of the S0 singlet energy at the T1 geometry, at the B3LYP/Lanl2DZ/PCM(Chloroform) level of theory.

B3LYP SP T1@T1.out: Single point calculation of the T1 triplet energy at the T1 geometry, at the B3LYP/Lanl2DZ/PCM(Chloroform) level of theory.

CLF OPT-T23 S&T.out: Optimization of T1 geometry by a TDDFT calculation at the B3LYP/Lanl2DZ/PCM(Chloroform) level of theory.

TDDFT B3LYP ACN.out: TDDFT (n = 200 singlet-singlet excitations) calculation at the B3LYP/Lanl2DZ/PCM(Acetonitrile) level of theory.

TDDFT B3LYP CLF.out: TDDFT (n = 200 singlet-singlet excitations) calculation at the B3LYP/Lanl2DZ/PCM(Chloroform) level of theory.

TDDFT B3LYP DCM.out: TDDFT (n = 200 singlet-singlet excitations) calculation at the B3LYP/Lanl2DZ/PCM(dichloromethane) level of theory.

TDDFT B3LYP EtOH.out: TDDFT (n = 200 singlet-singlet excitations) calculation at the B3LYP/Lanl2DZ/PCM(Ethanol) level of theory.

TDDFT B3LYP H2O.out: TDDFT (n = 200 singlet-singlet excitations) calculation at the B3LYP/Lanl2DZ/PCM(Water) level of theory.

TDDFT B3LYP MeOH.out: TDDFT (n = 200 singlet-singlet excitations) calculation at the B3LYP/Lanl2DZ/PCM(Methanol) level of theory.

[1] N. O'Boyle, GaussSum 2.2.5 program documentation (http://gausssum.sourceforge.net/GaussSum_UVVis_Convolution.pdf).