

# Controlling NIR Band Shapes, Intensity and Position by Bridge Variation in Diruthenium Complexes

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1,4-Benzoquinones are interesting molecules that play an important role in biological processes like photosynthesis and cellular respiration. Their ability to reversibly take up one or two electrons makes them efficient electron shuttles with their redox potentials depending on the substituents at the quinone ring.<sup>[1]</sup> To explore this dependence of the electronic properties, a number of symmetric and asymmetric 2,5-substituted 1,4-benzoquinones was synthesized and used as bridging ligands for binuclear Ru complexes.<sup>[2]</sup> Mononuclear complexes were synthesized for comparison.

2,5-Dihydroxy-1,4-benzoquinone ( $L^1H_2$ ), 2-*N*-mesitylamino-5-hydroxy-1,4-benzoquinone ( $L^2H_2$ ), 2,5-di-*N*-mesitylamino-1,4-benzoquinone ( $L^3H_2$ ) and 2-*N*-mesitylamino-5-amino-1,4-benzoquinone ( $L^4H_2$ ) were deprotonated and reacted with 1 or 0.5 eq of  $[\{(TPA)Ru\}_2(\mu-Cl)_2](ClO_4)_2$  (TPA = tris(2-pyridylmethyl)amine) yielding the corresponding dinuclear (**1 - 4**) and mononuclear (**5**) complexes  $[\{(TPA)Ru\}_2(\mu-L)](ClO_4)_2$ . Cyclic voltammetry measurements showed two reversible oxidations and at least one reversible reduction for **1 - 4**, whereas for **5** only one oxidation and two reductions were observed. With an increasing number of aminosubstituents at the bridging ligand ( $L^1H_2 < L^2H_2 < L^3H_2 = L^4H_2$ ) the redoxpotentials of the complexes shift to more anodic values and the potential difference  $\Delta E_{Ox/Red}$  between first oxidation and first reduction grows.

The one-electron oxidised form of all dinuclear complexes shows absorptions in the NIR region which are assigned to an Inter Valence Charge Transfer (IVCT) transition. Such transitions are absent in the mononuclear complex justifying their assignment as IVCT transitions. Further proof of this comes from EPR spectroscopy which shows metal-centered spin. Whereas the complexes with a symmetrical bridging ligand show NIR bands that are narrow and asymmetric (Fig. 1, top), the complexes with an asymmetric bridge show NIR bands that are symmetric and broad (Fig. 1, bottom).

Thus a switching between class III and class II mixed-valent systems can be achieved by simple substitutions in the bridge. Furthermore the position as well as the intensities of the NIR bands can be systematically controlled by the number of nitrogen substituents on the bridge. The NIR absorptions can be switched on and off by a simple one-electron process at relatively low potentials. Chromophors having such strong switchable absorptions can have use in optical fibres for electro-optical switching.

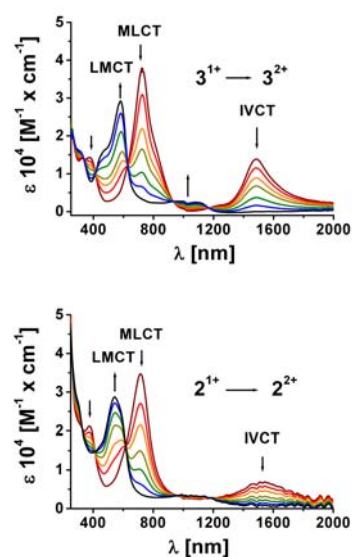


Fig. 1

- [1] D. Schweinfurth, F. Weisser, B. Sarkar, *Nachrichten aus der Chemie*, **2009**, 57, 862.  
[2] F. Weisser, D. Schweinfurth, R. Huebner, R. Pattacini, B. Sarkar, *Chem. Eur. J.*, submitted.