Supplementary material to the paper entitled

Oxidative C—H and C—C bond cleavage by a (2,2'-bipyridine)copper(I) chloride complex

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Preparation of the complexes 1 and 2:

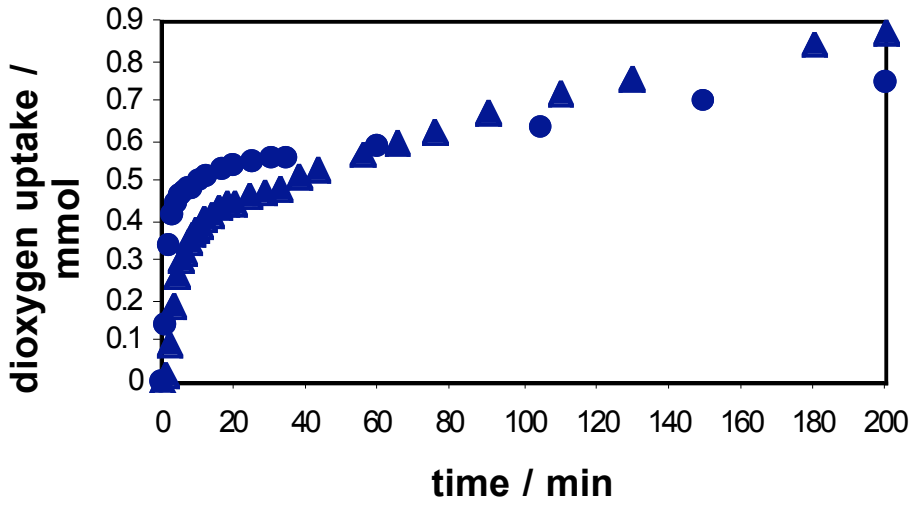
0.5 mmol (111 mg) dtbcH_2 (3,5-di-*tert*-butilcatechol), and 0.5 mmol (78.1 mg) bpy (2,2'-bipyridine) was mixed and dissolved in 5 ml acetonitrile at room temperature under dioxygen atmosphere in a 50 ml thermostated reaction vessel. This vessel was attached to a dioxygen filled burette. The measurement of the dioxygen absorption was started after adding 0.5 mmol (50 mg) CuCl to the solution. The color of the mixture turned from colorless to brown and after 2-3 minutes to green. Finally, when no more dioxygen absorption was observed the filtration resulted in green powder as a mixture of **1** and $CuCl_2$(bpy) in a stoichiometric reaction. Yield: 111 mg. After recrystallization from water we obtained a blue complex (**1**) and a green complex [$CuCl_2$(bpy)] as crystals in case of acetonitrile as solvent. The yield of [Cu(bpy)(ox)] (**1**): 70 mg (46%); IR and X-ray data similar with the literature data (CCDC 644887). Anal. Calcd for $C_{12}H_8N_2CuO_4$: C, 46.8; H, 2.6; N, 9.1. Found: C, 46.6; H, 2.5; N, 8.9. Yield of [Cu(bpy)Cl_2]: 28 mg (19%), structure proved by x-ray determination and identical with literature data, and IR (KBr): 1610, 1601, 1445, 1317, 778 cm^{-1}. EPR: $g_{\|}$ = 2.173, $g_{\perp}$ = 2.070 at 77 K.

Using the same method with propionitrile as the solvent the product was a green powder (116 mg). After recrystallization from water blue [Cu(bpy)(mal)(H_2O)] (**2**) was obtained and

its structure determined by X-ray diffraction. CCDC 257304. Yield: 85 mg (42%), UV/Vis (DMSO): λ (log ε = 260 (3.78), 302 (4.03), 423 (1.61); IR (KBr): ν= 1645, 1601, 1446, 1374, 776 cm^{-1}; EPR: $g_{\|}$ = 2.270, $g_{\perp}$ = 2.050 and $^{Cu}A_{\|}$ = 177 G at 77 K; mp.: 266ºC. Anal. Calcd for $C_{18}H_{20}N_2CuO_5$: C, 53.0; H, 4.9; N, 6.9. Found: C, 52.8; H, 4.7; N, 6.7. As the byproduct $[CuCl_2(bpy)]$ as green crystals were obtained. Yield: 25 mg (17%). IR (KBr): ν = 1610, 1601, 1445, 1317, 778 cm^{-1}.

If other nitriles such as isobutironitrile, propionitrile or benzilnitrile were used compound 2 was obtained in yields of 48, 43, and 39% respectively.

SFigure 1. The dioxygen uptakes of the reactions of $dtbcH_2$, bpy, CuCl in MeCN (▲) and EtCN (●). Solvent 5 ml, [CuCl] = [bpy] = $dtbcH_2$] = 0.5 mmol; 25°C, 1 bar O_2.



SFigure 2. UV-Vis spectra of the reaction of $dtbcH_2$, bpy, CuCl in MeCN. Solvent 45 ml, [CuCl] = [bpy] = $dtbcH_2$] = 0.5 mmol; 25°C, 1 bar air. The increase (red) and decrease (blue) of 3,5-di-*tert*-butyl-1,2-benzoquinone.