

## Mechanosynthesized Copper (I) complex based initiating systems for redox polymerization: towards upgraded oxidizing and reducing agents

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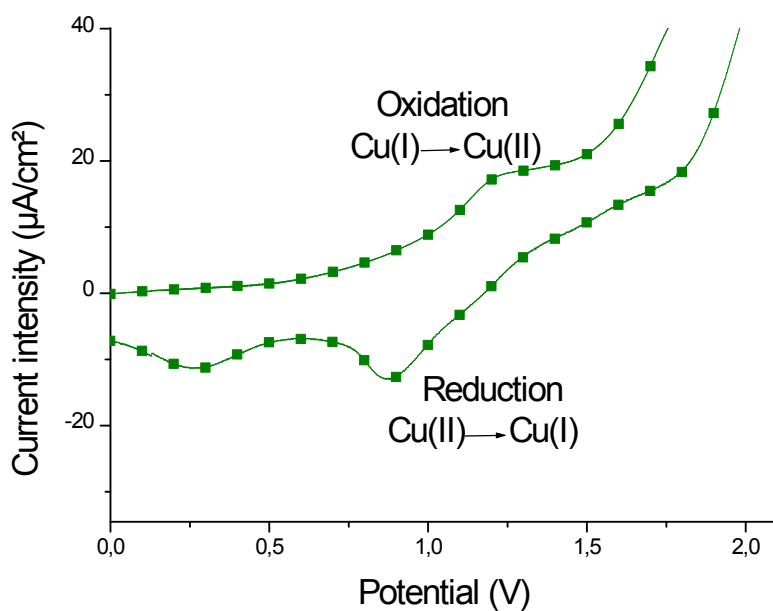


Figure S1: Cyclic voltammogram of 3 mM M-CuC-1Cl in DCM under air, sweeping rate 0.1 V/S, potential vs SCE.

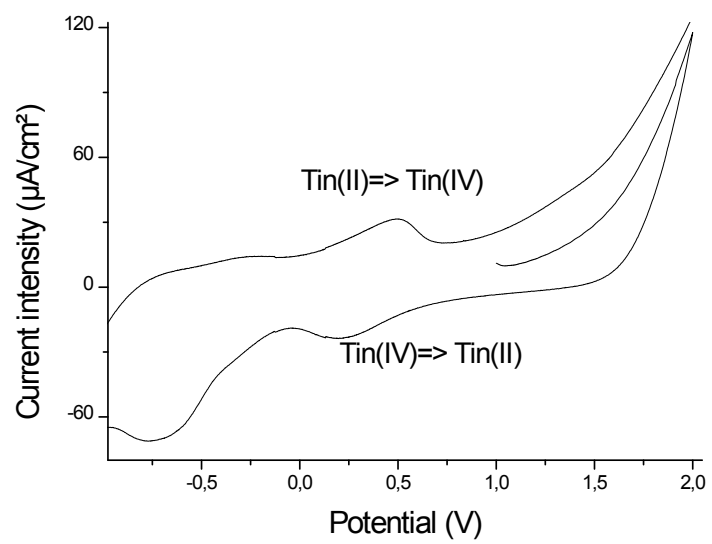
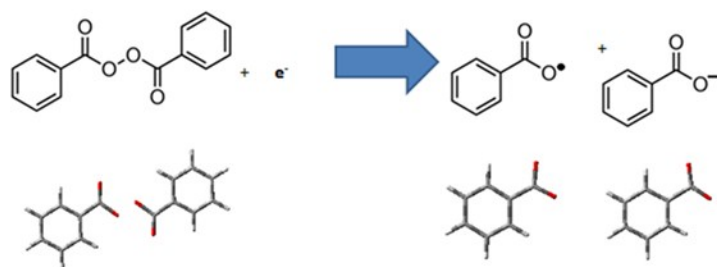


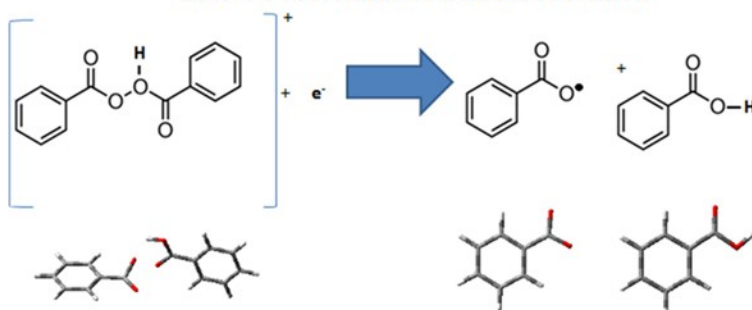
Figure S2: Cyclic voltammogram of 10 mM Tin(II) in DCM under nitrogen, sweeping rate 0.2 V/S, potential vs SCE.

### BPO / Normal redox dissociation



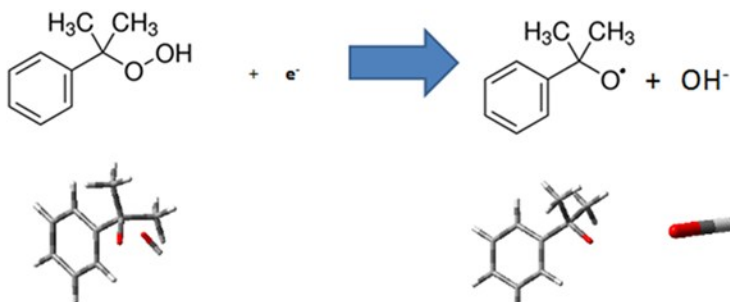
$$\Delta H = -38.98 \text{ kcal mol}^{-1}$$

### BPO / Protonated redox dissociation



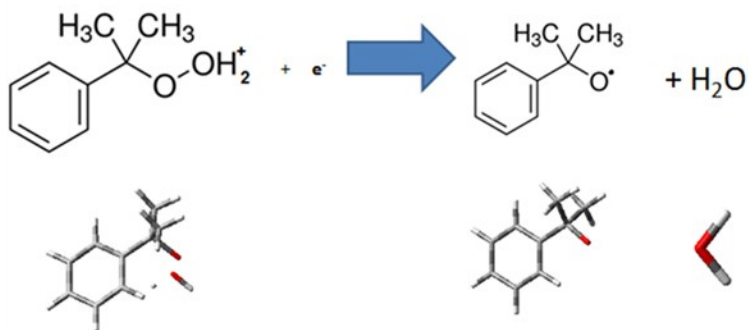
$$\Delta H = -180.72 \text{ kcal mol}^{-1}$$

### CHP / Normal redox dissociation



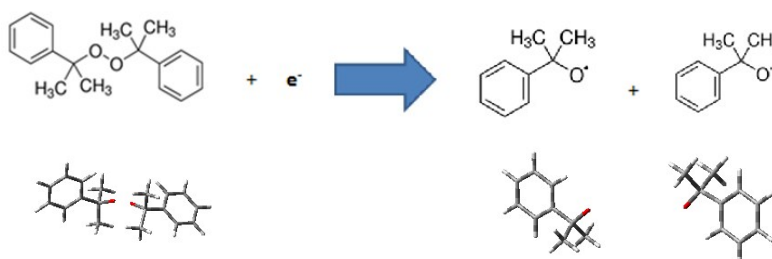
$$\Delta H = 44.82 \text{ kcal mol}^{-1}$$

### CHP / Protonated redox decomposition



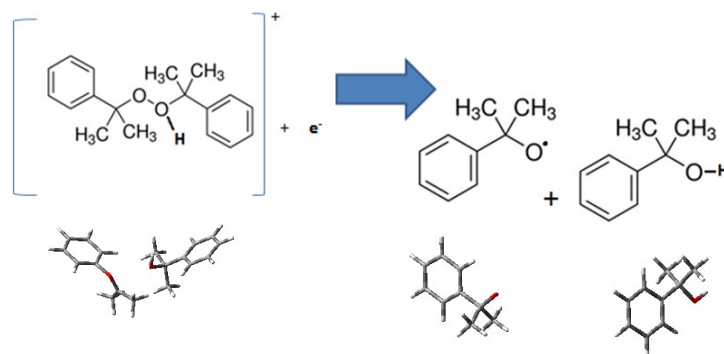
$$\Delta H = -190.83 \text{ kcal mol}^{-1}$$

### DCP / Normal redox decomposition



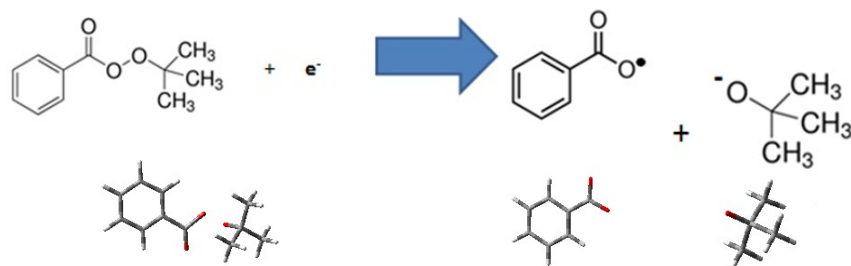
$\Delta H = -1.14 \text{ kcal mol}^{-1}$

### DCP / Protonated redox decomposition



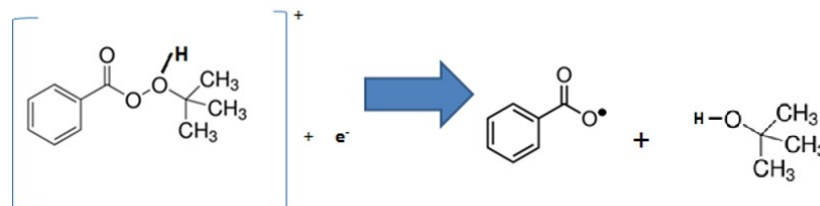
$\Delta H = -112.13 \text{ kcal mol}^{-1}$

### tBu-PBz / Normal redox decomposition



$\Delta H = 10.86 \text{ kcal mol}^{-1}$

### tBu-PBz / Protonated redox decomposition



$\Delta H = -164.13 \text{ kcal mol}^{-1}$

Figure S3: Optimized structures and reaction enthalpies of the redox and protonated redox decomposition reactions for BPO, CHP, DCP and tBu-PBz. Computed at UB3LYP/LANL2DZ level.