

Supplementary Information:

Stable copper acetylacetonate-based oxidizing agents in redox (NIR photoactivated) polymerization: an opportunity for one pot *grafting from* approach and example on a 3D printed object

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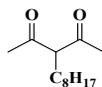
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Synthesis of Copper acetylacetonates (Cu(C8-acac)₂, Cu(C8-acac)(2dppba), Cu(tBu-acac)₂, Cu(DBz-acac)₂, Cu(BzC6-acac)₂)

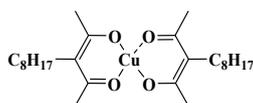
All reagents and solvents were purchased from Aldrich or Alfa Aesar and used as received without further purification. Mass spectroscopy was performed by the Spectropole of Aix-Marseille University. ESI mass spectral analyses were recorded with a 3200 QTRAP (Applied Biosystems SCIEX) mass spectrometer. The HRMS mass spectral analysis was performed with a QStar Elite (Applied Biosystems SCIEX) mass spectrometer. Elemental analyses were recorded with a Thermo Finnigan EA 1112 elemental analysis apparatus driven by the Eager 300 software. ¹H and ¹³C NMR spectra were determined at room temperature in 5 mm o.d. tubes on a Bruker Avance 400 spectrometer of the Spectropole: ¹H (400 MHz) and ¹³C (100 MHz). The ¹H chemical shifts were referenced to the solvent peaks CDCl₃ (7.26 ppm), DMSO (2.49 ppm) and the ¹³C chemical shifts were referenced to the solvent peak CDCl₃ (77.0 ppm), DMSO (49.5 ppm). All these copper acetylacetonates were prepared with analytical purity up to accepted standards for new organic compounds (>98%) which was checked by high field NMR analysis.

Synthesis of 3-octylpentane-2,4-dione



A solution of 1-bromooctane (1.84 g, 1.65 mL, 9.55 mmol), potassium carbonate (1.33 g, 9.62 mmol) and acetylacetone (0.96 g, 0.98 mL, 9.59 mmol) and a few crystals of 18-crown-6 were suspended in 30 mL dry acetone. The reaction mixture was refluxed overnight. The solution was filtered while hot, and the solvent removed under reduced pressure. Water was added and the solution was extracted with DCM, the organic phases were combined, dried over magnesium sulfate and the solvent removed under reduced pressure. The residue was purified by silicagel chromatography means using successively: hexanes to removed octanol and bromooctane, a mixture of hexanes/DCM to get the expected molecule ($m_{th} = 1.58$ g, 78% yield) as a yellowish oil and pure DCM to elute the side-product: (*O*-alkylation). NMR data are consistent with those previously reported in the literature [Inorg. Chem. 2017, 56, 4555–4567]. ^1H NMR (CDCl_3) δ 0.87 (t, 3H, $J = 7.2$ Hz, 3H), 0.88 (t, 3H, $J = 7.2$ Hz), 1.20-1.28 (m, 24H), 1.75–1.84 (m, 2H), 2.11 (s, 6H), 2.14 (s, 6H), 2.14–2.21 (m, 2H), 3.59 (t, 1H, $J = 7.2$ Hz), 16.74 (s, 1H); ^{13}C NMR (CDCl_3) δ 14.4, 23.2, 28.1, 28.2, 28.8, 29.6, 29.8, 29.85, 29.9, 30.0, 30.1, 30.2, 31.2, 32.4, 32.5, 69.1, 111.2, 191.6, 205.0; HRMS (ESI MS) m/z : theor: 212.1776 found: 212.1779 ($[\text{M}]^+$ detected).

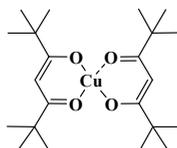
Synthesis of $\text{Cu}(\text{C8-acac})_2$



Copper acetate (1.27 g, 6.35 mmol) was added to 3-octylpentane-2,4-dione (2.70 g, 12.7 mmol) in a mixture of methanol (100 mL) and DCM (20 mL) while stirring. The solution was stirred at room temperature overnight. A precipitate formed. It was filtered off, washed several times with methanol

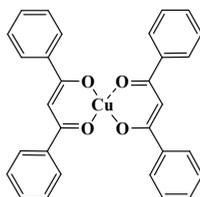
and dried under vacuum. Anal. Calc. for $C_{26}H_{46}CuO_4$: C, 64.2; H, 9.5; O, 13.2 Found: C, 64.3; H, 9.4; N, 13.3%; HRMS (ESI MS) m/z : theor: 485.2692 found: 485.2695 ($[M]^+$ detected).

Synthesis of $Cu(tBu-acac)_2$



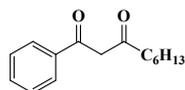
Copper acetate (1.27 g, 6.35 mmol) was added to 2,2,6,6-tetramethylheptane-3,5-dione (2.34 g, 2.63 mL, 12.7 mmol) in a mixture of methanol (100 mL) and DCM (20 mL) while stirring. The solution was stirred at room temperature overnight. A precipitate formed. It was filtered off, washed several times with methanol and dried under vacuum. Anal. Calc. for $C_{22}H_{38}CuO_4$: C, 61.4; H, 8.9; O, 14.9 Found: C, 61.6; H, 8.9; N, 14.7%; HRMS (ESI MS) m/z : theor: 430.0880 found: 430.0884 ($[M]^+$ detected).

Synthesis of $Cu(DBZ-acac)_2$



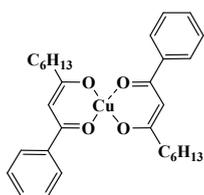
Copper acetate (1.27 g, 6.35 mmol) was added to dibenzoylmethane (2.84 g, 12.7 mmol) in a mixture of methanol (100 mL) and DCM (20 mL) while stirring. The solution was stirred at room temperature overnight. A precipitate formed. It was filtered off, washed several times with methanol and dried under vacuum (3.07 g, 95% yield). Anal. Calc. for $C_{30}H_{22}CuO_4$: C, 70.6; H, 4.3; O, 12.5 Found: C, 70.5; H, 4.3; N, 12.5%; HRMS (ESI MS) m/z : theor: 509.0814 found: 509.0816 ($[M]^+$ detected).

Synthesis of 1-phenylnonane-1,3-dione



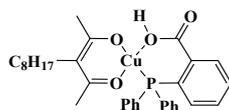
Acetophenone (1.20 g, 1.16 mL, 10 mmol) was dissolved in dry THF (10 mL). The solution was cooled to 0°C and lithium diisopropylamide (LDA) (5.4 mL 2M, 10.8 mmol) was added. A color change to clear orange showed that a slight excess of LDA was added. The solution was allowed to stir for 10 min before ethyl heptanoate (1.58 g, 1.82 mL, 10 mmol) was slowly added into the solution at 0°C while stirring. The reaction mixture was stirred overnight under N₂ atmosphere. Ether (30 mL) was added into the reaction mixture and stirred for 20 min. The resulting precipitate was filtered and washed with ether (2 × 30 mL). Ether (20 mL) was added to the precipitate, and 0.3 M HCl (20 mL) dropped by while stirring till a pH lower than 4 was reached. The product was extracted with ether (2 × 50 mL). The combined ether extracts were dried with anhydrous MgSO₄ and removed by evaporation. Silica gel column chromatography was used to purify the product (1.58 g, 68% yield). ¹H NMR (CDCl₃) δ 0.95 (t, 3H, J = 7.2 Hz), 1.30-1.37 (m, 6H), 1.61-1.78 (m, 2H), 2.46 (t, 2H, J = 7.6 Hz), 6.19 (s, 1H), 7.40-7.47 (m, 2H), 7.49-7.53 (m, 1H), 7.87-7.90 (m, 2H), 16.28 (s, 1H); ¹³C NMR (CDCl₃) δ 14.3, 22.8, 22.9, 23.0, 23.1, 26.0, 31.9, 39.3, 96.6, 127.8, 128.9, 132.7, 135.5, 183.7, 197.4; HRMS (ESI MS) m/z: theor: 232.1463 found: 232.1466 ([M]⁺ detected).

Synthesis of Cu(BZC6-acac)₂



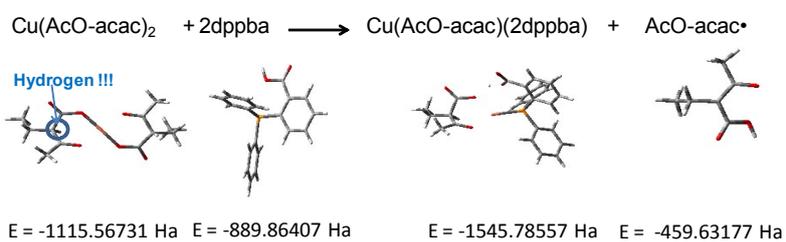
Copper acetate (1.27 g, 6.35 mmol) was added to 1-phenylnonane-1,3-dione (2.95 g, 12.7 mmol) in a mixture of methanol (100 mL) and DCM (20 mL) while stirring. The solution was stirred at room temperature overnight. A precipitate formed. It was filtered off, washed several times with methanol and dried under vacuum. Anal. Calc. for $C_{30}H_{38}CuO_4$: C, 68.5; H, 7.3; O, 12.1 Found: C, 68.5; H, 7.2; N, 12.3%; HRMS (ESI MS) m/z : theor: 525.2066 found: 525.2067 ($[M]^+$ detected).

Synthesis of Cu(C8-acac)(2dppba)

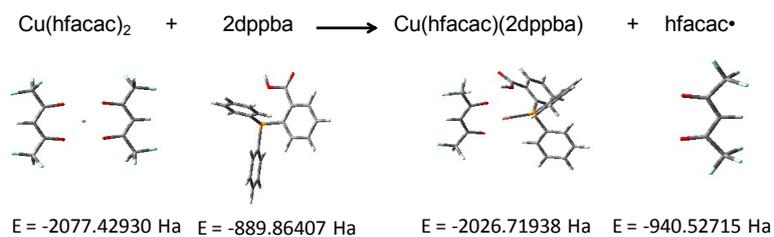


$Cu(C8-acac)_2$ copper acetylacetonate (972 mg, 2 mmol) and 2-(diphenylphosphino)benzoic acid (612 mg, 2 mmol) were suspended in THF (20 mL) and stirring was maintained at room temperature overnight. A precipitate formed. It was filtered off, washed several times with methanol and dried under vacuum. Anal. Calc. for $C_{32}H_{38}CuO_4P$: C, 66.1; H, 6.6; O, 11.0 Found: C, 66.0; H, 6.8; N, 11.2%; HRMS (ESI MS) m/z : theor: 580.1804 found: 580.1801 ($[M]^+$ detected).

$$\Delta H = 8.94 \text{ kcal.mol}^{-1}$$



$$\Delta H = 29.39 \text{ kcal.mol}^{-1}$$



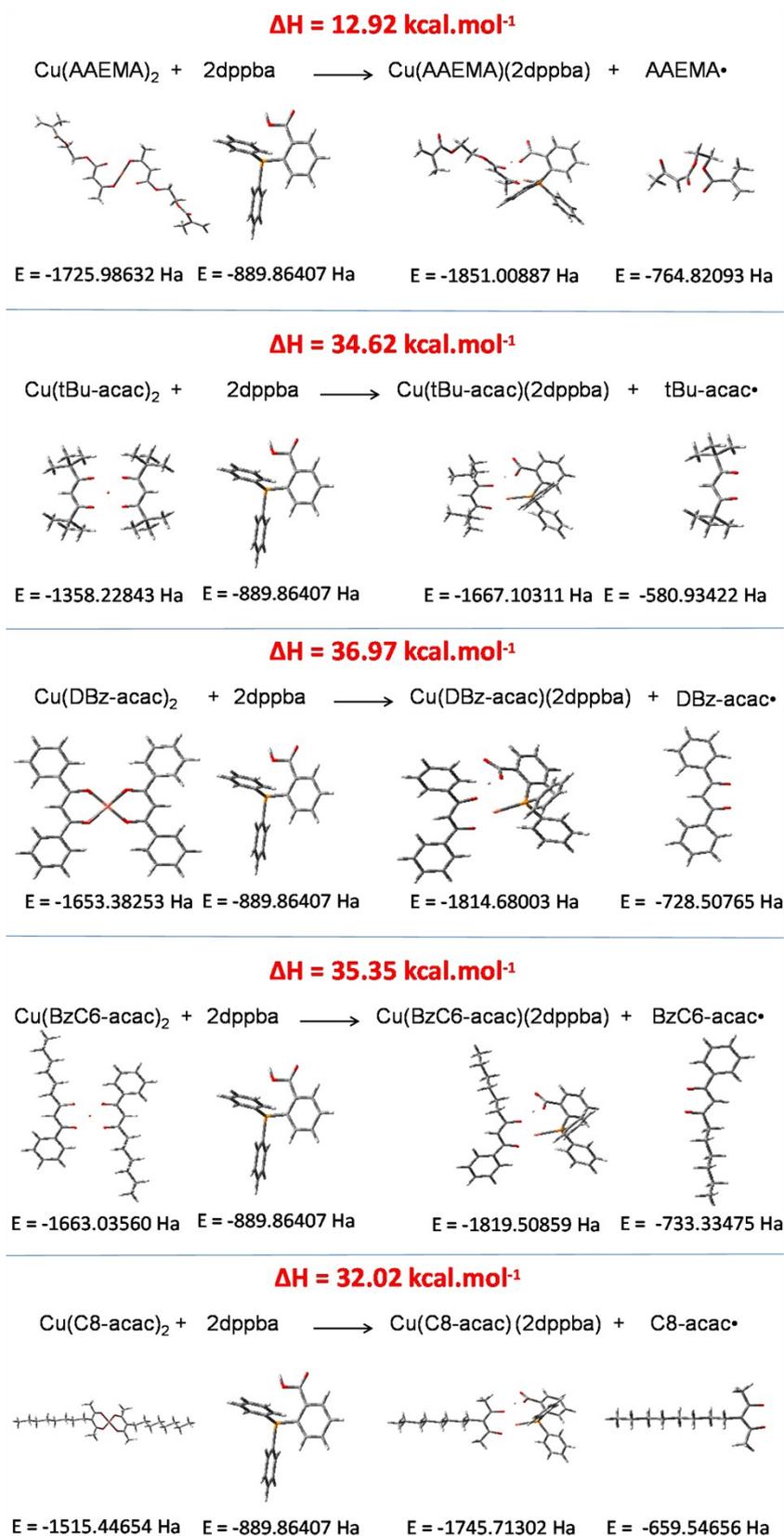


Figure S1. Optimized structures and reaction enthalpies of the MABLI reactions for various Copper acetylacetonates reacting with 2dppba. Computed at UB3LYP/LANL2DZ level.

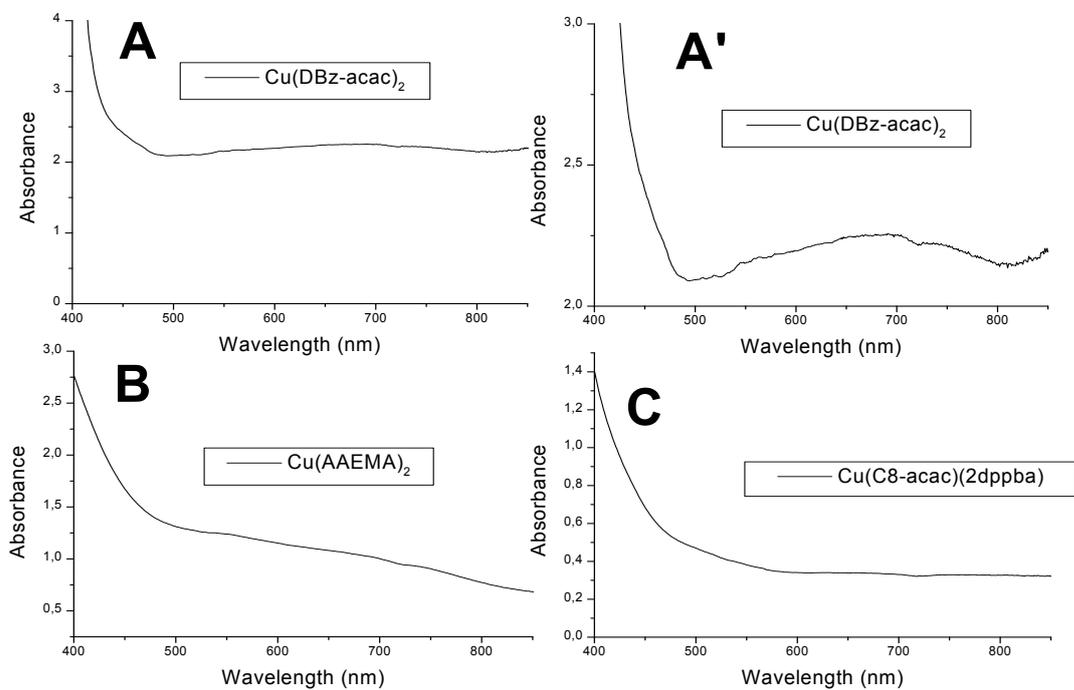


Figure S2. UV-Vis spectrometry in DCM for Copper acetylacetonates showing partial solubility. **A; A'** $\text{Cu}(\text{DBz-acac})_2=4.15$ g/L. **B.** $\text{Cu}(\text{AAEMA})_2=3.20$ g/L. **C.** $\text{Cu}(\text{C8-acac})(2\text{dppba})=3.38$ g/L.