

An effective trigger for energy release of vinylheptafulvene-based solar heat batteries

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Supporting Information

General methods

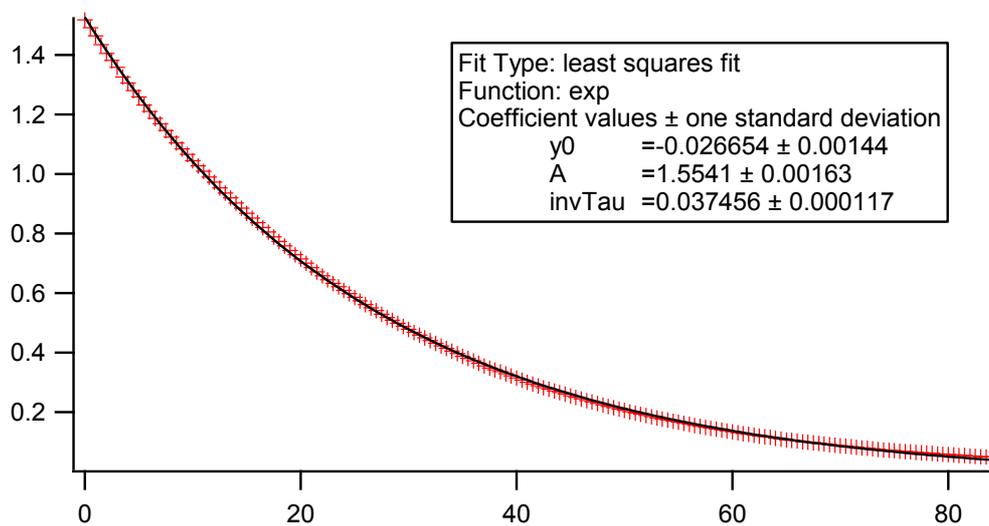
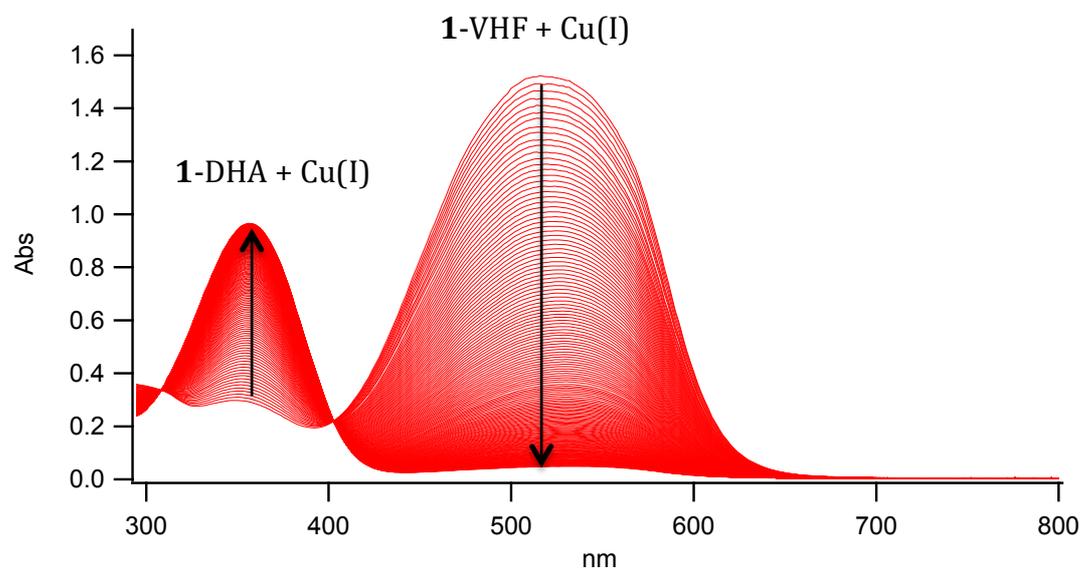
All the UV-Vis absorption spectra experiments have been repeated three times. The sample containing a solution of the DHA derivative (ca. 10^{-5} M) in dichloromethane or acetone has been irradiated at its maximum wavelength (365 nm) using a 150-W Xenon arc lamp equipped with a monochromator until no further changes in the spectrum were detected (ca. 1-2 min for DHA **1-3**, ca. 10 min for double DHA **4** and ca. 1 h for the DHA macrocycle **5**). Then a solution of Cu(I) salt in dichloromethane or acetone was added (0.5-3 equiv. per DHA unit) and UV-Vis absorption spectra were recorded within time with a Cary50 Bio UV-Visible spectrophotometer equipped with a single cell Peltier thermostat for temperature control. $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$ and $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ were used for the studies as source of Cu(I) without noticing relevant differences. The decay of the absorbance of the VHF species at its maximum wavelength was plotted against time, and the data were elaborated with a least squares fitting exponential or double exponential depending on the system. From the equation the rate constant and the half-life of the VHF species were determined.

Contents

- 1) UV-Vis absorption spectra recorded during the thermal back reaction of **1**-VHF, **4**-VHF-VHF and **5**-VHF-VHF in DCM in the presence of Cu(I) and corresponding decay of absorption at specific wavelengths.
- 2) UV-Vis absorption spectra in DCM of **4**-DHA-DHA and **4**-VHF-VHF before and after addition of Cu(I).
- 3) UV-Vis absorption spectra recorded during the thermal back reaction of **2**-VHF in acetone in the presence of Cu(I) and corresponding decay of absorption at specific wavelengths.
- 4) Movie of addition of excess of ethylenediamine to the **5**-VHF-VHF + Cu(I) solution.
- 5) Recyclability experiments
- 6) Figure S1: polarized TS structure.

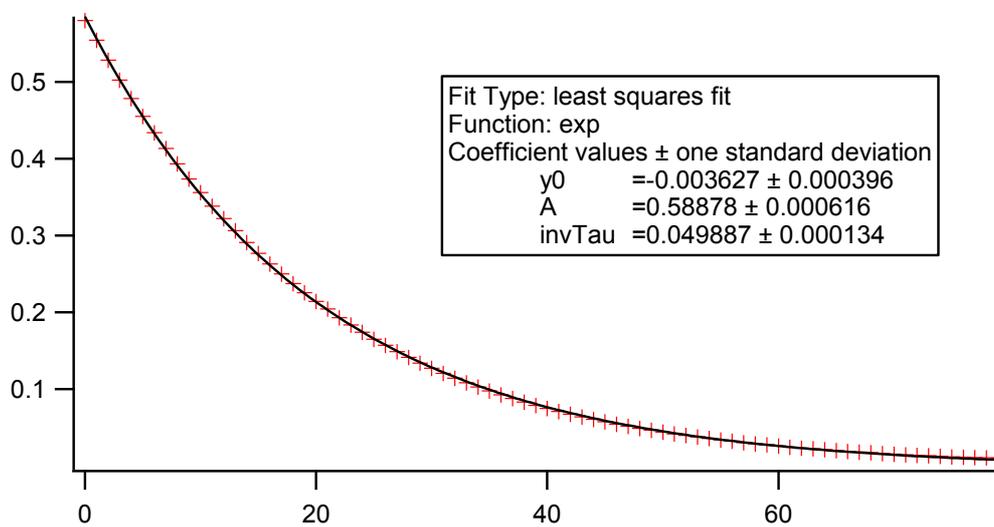
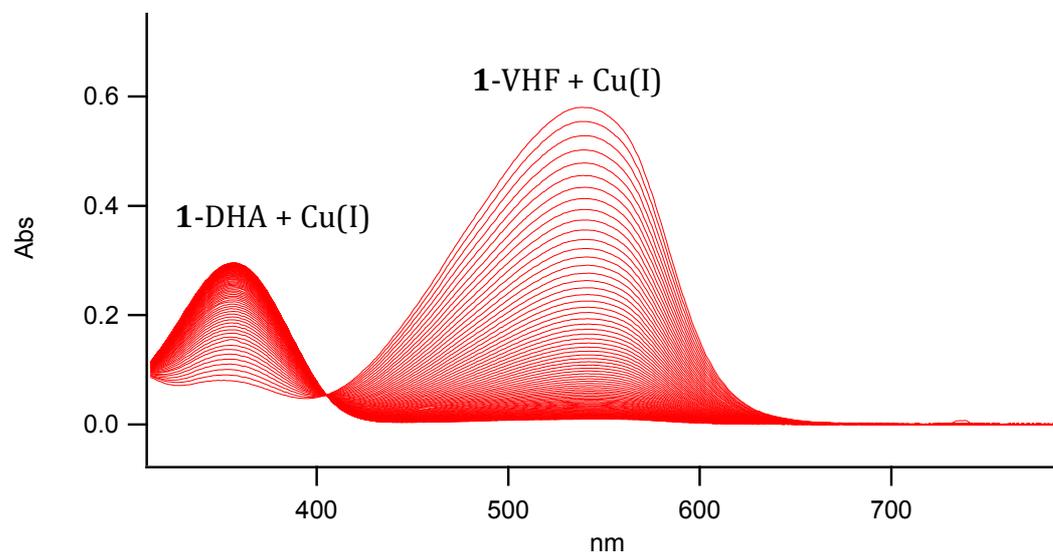
Thermal back reaction of **1-VHF** to **1-DHA** upon addition of **1 equiv. of Cu(I)** (TBR of the complex VHF·Cu(I) to DHA·Cu(I)) in **DCM** at 25 °C and fit of the absorbance at 522 nm.

Half-life: 18 min



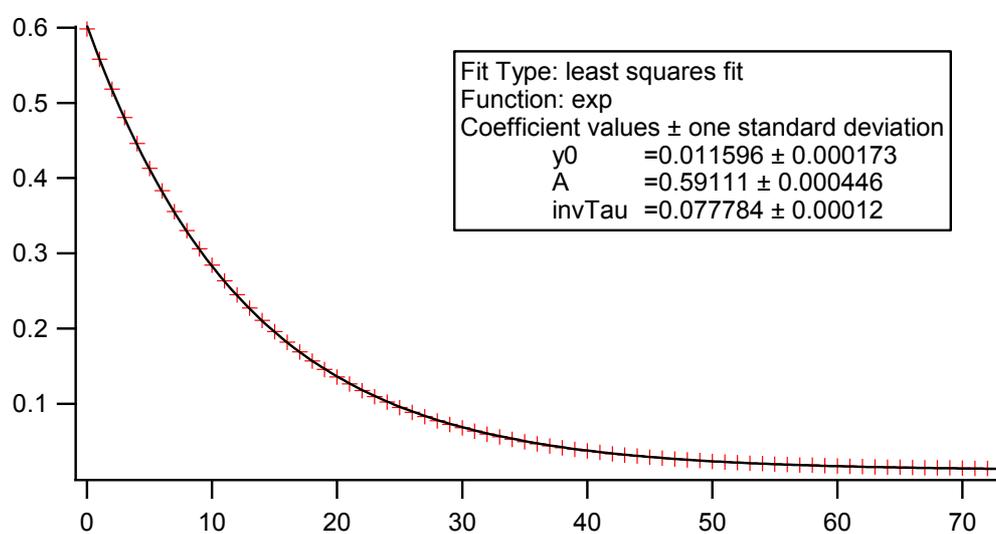
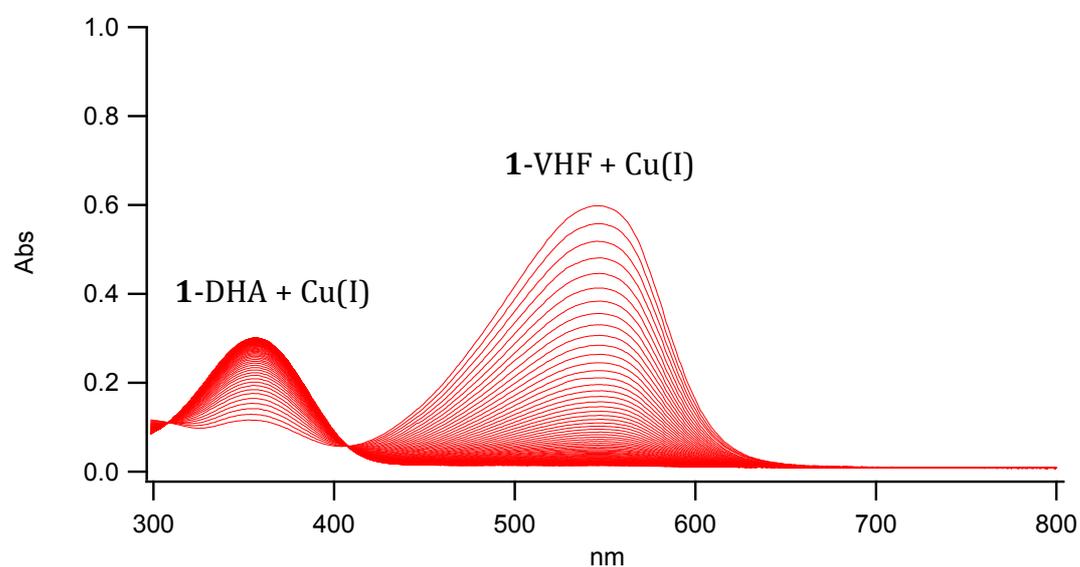
Thermal back reaction of VHF to DHA upon addition of **3 equiv. of Cu(I)** (TBR of the complex VHF·Cu(I) to DHA·Cu(I)) in **DCM** at 25 °C and fit of the absorbance at 540 nm.

Half-life: 14 min



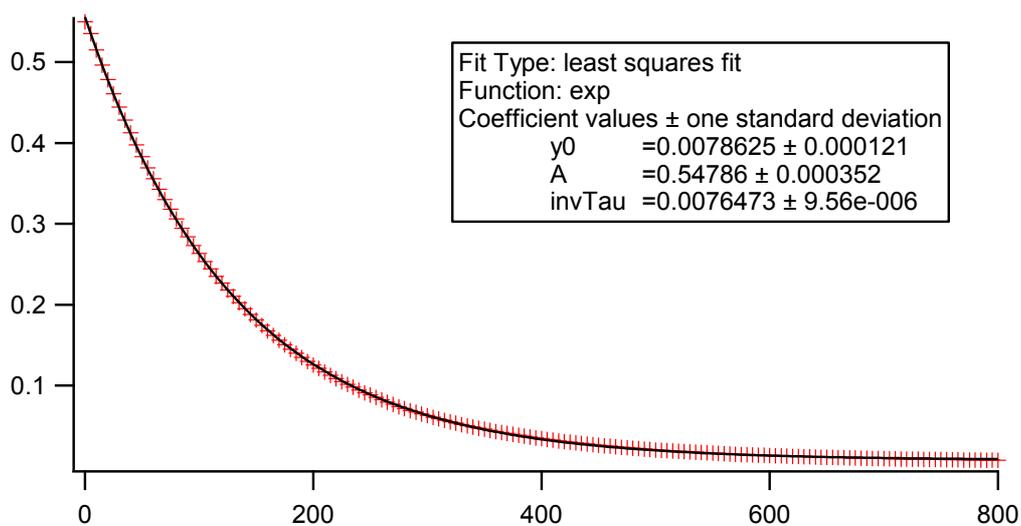
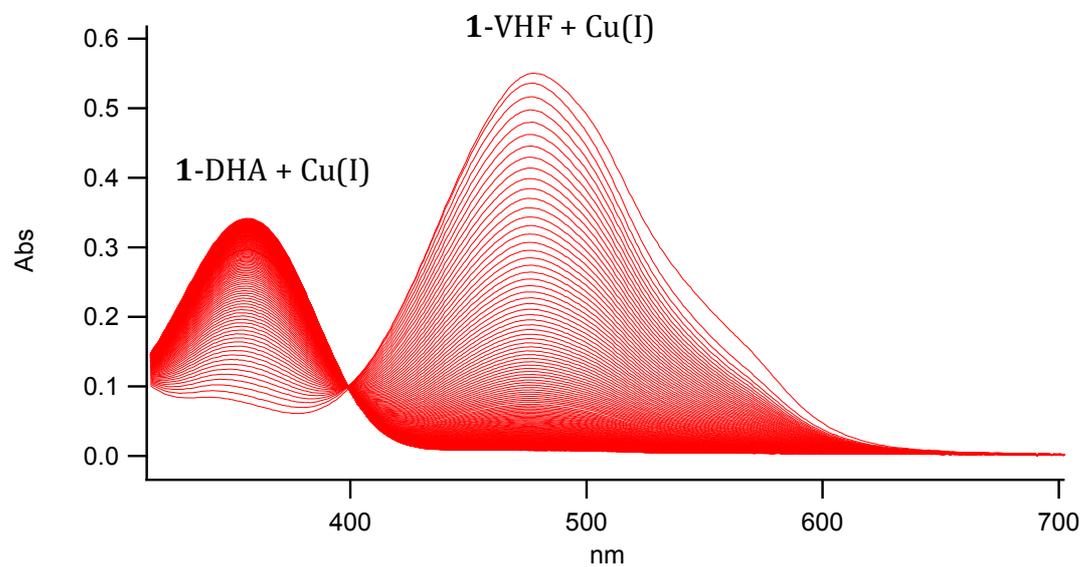
Thermal back reaction of VHF to DHA upon addition of **10 equiv. of Cu(I)** (TBR of the complex VHF·Cu(I) to DHA·Cu(I)) in **DCM** at 25 °C and fit of the absorbance at 545 nm.

Half-life: 9 min

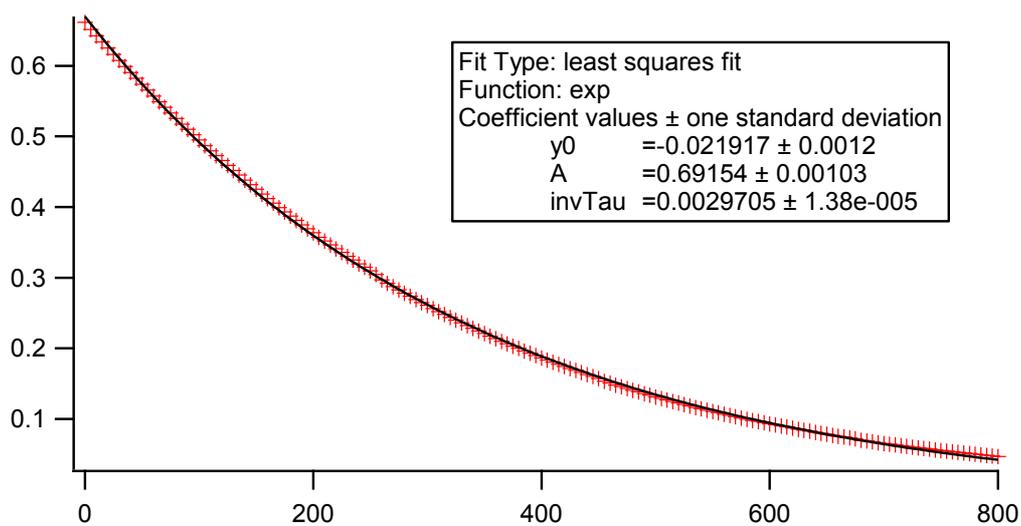
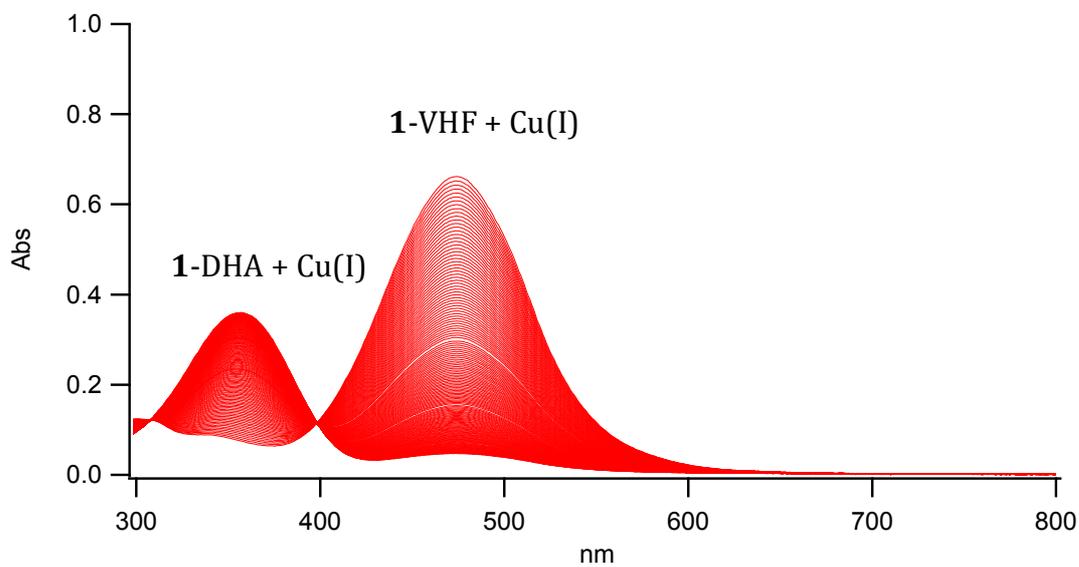


Thermal back reaction of VHF to DHA upon addition of **0.2 equiv. of Cu(I)** (TBR of the complex VHF-Cu(I) to DHA-Cu(I)) in **DCM** at 25 °C and fit of the absorbance at 479 nm.

Half-life: 91 min

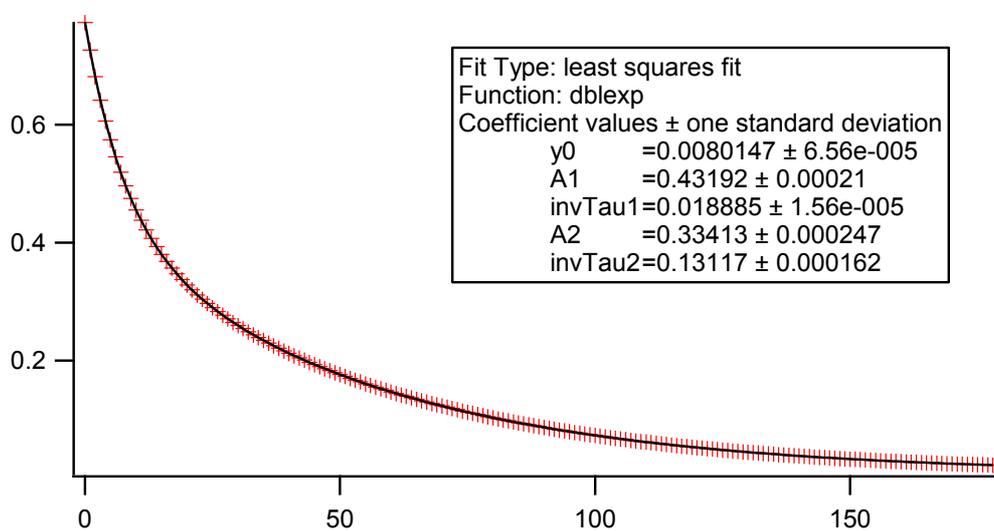
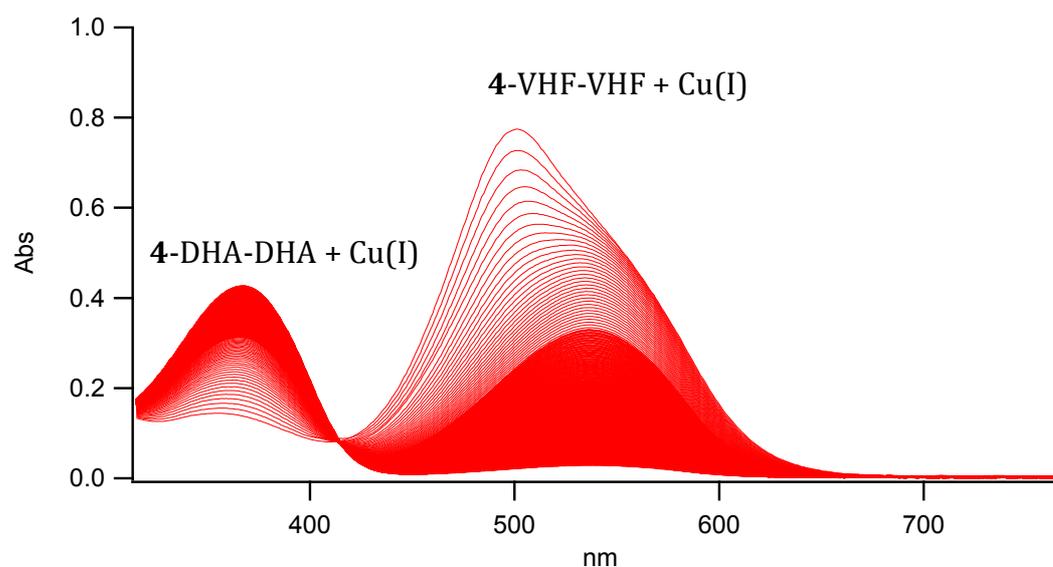


Second-cycle with 0.2 equiv. of Cu(I), half-life: 223 min



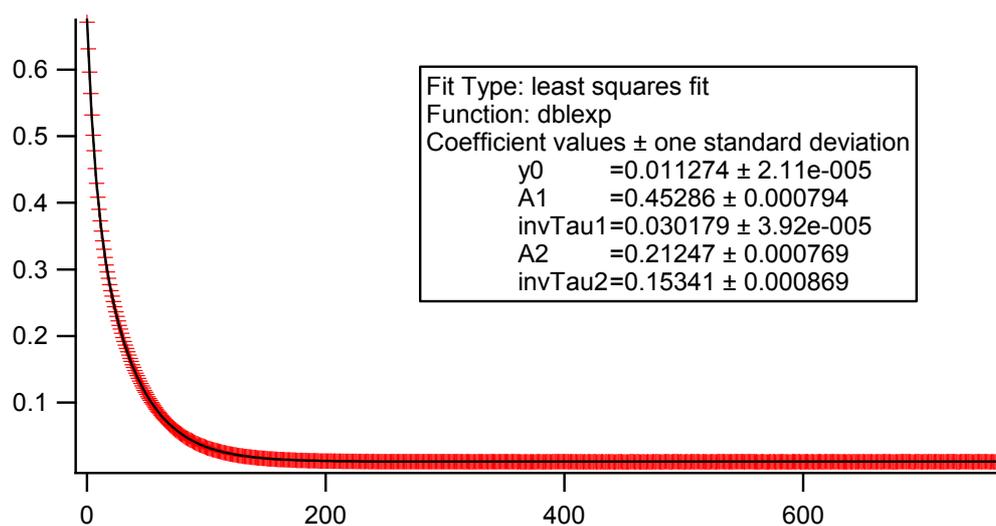
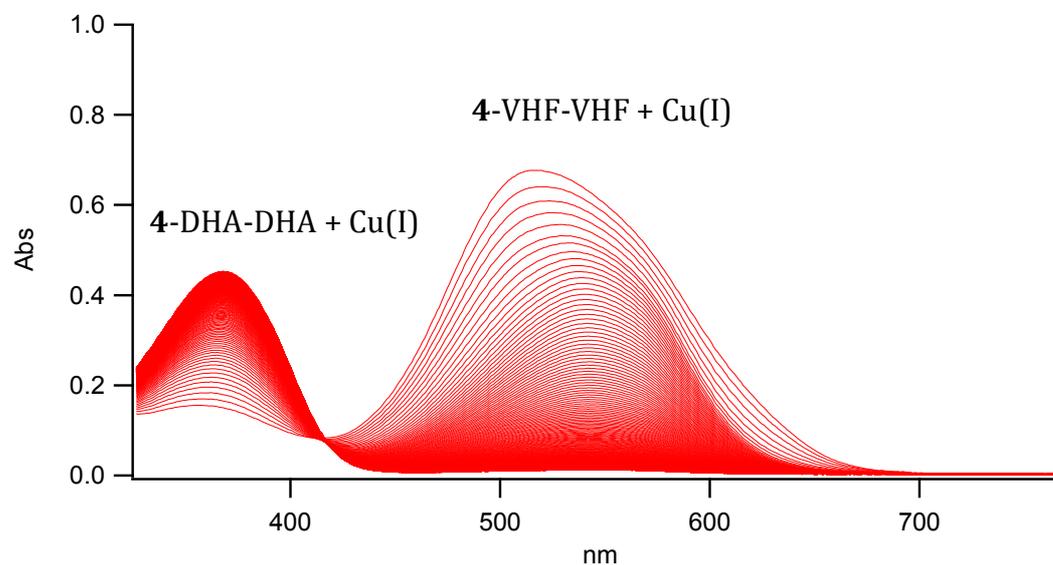
Thermal back reaction of 4-VHF-VHF to 4-DHA-DHA upon addition of **1 equiv. of Cu(I) per DHA unit** in DCM at 25 °C and fit of the absorbance at 495 nm with double exponential function.

Half-lives: 5 min, 38 min



Thermal back reaction of **4-VHF-VHF** to **4-DHA-DHA** upon addition of **2.7 equiv. of Cu(I)** in **DCM per DHA unit** at 25 °C and fit of the absorbance at 510 nm with double exponential function.

Half-lives: 5 min, 23 min



Thermal back reaction of **4-VHF-VHF** to **4-DHA-DHA** upon addition of **0.5 equiv. of Cu(I)** in **DCM per DHA unit** at 25 °C and fit of the absorbance at 495 nm with double exponential function.

Half-lives: 9 min, 67 min

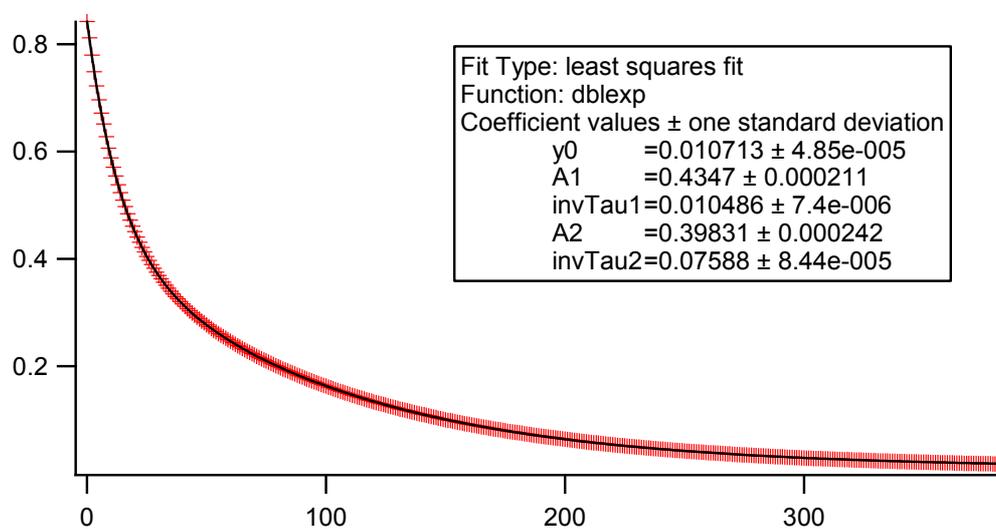
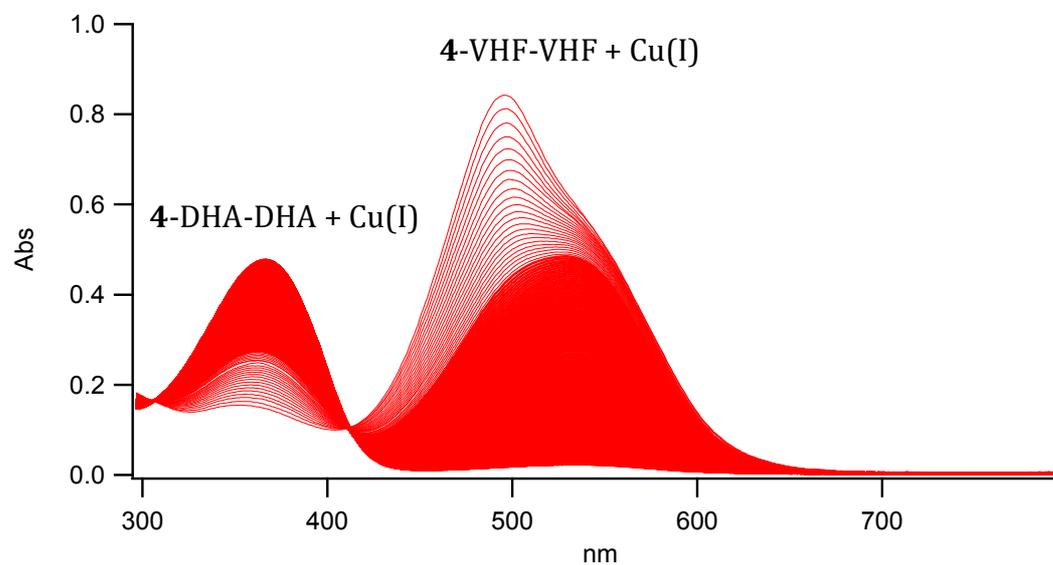


Figure S1. UV-Vis absorption spectra in DCM at 25 °C of **4-DHA-DHA** (black), **4-VHF-VHF** (red), **4-VHF-VHF** after addition 0.5 equiv. per DHA unit of Cu(I) (violet), showing the redshift from 470 nm to 495 nm of the VHF maximum.

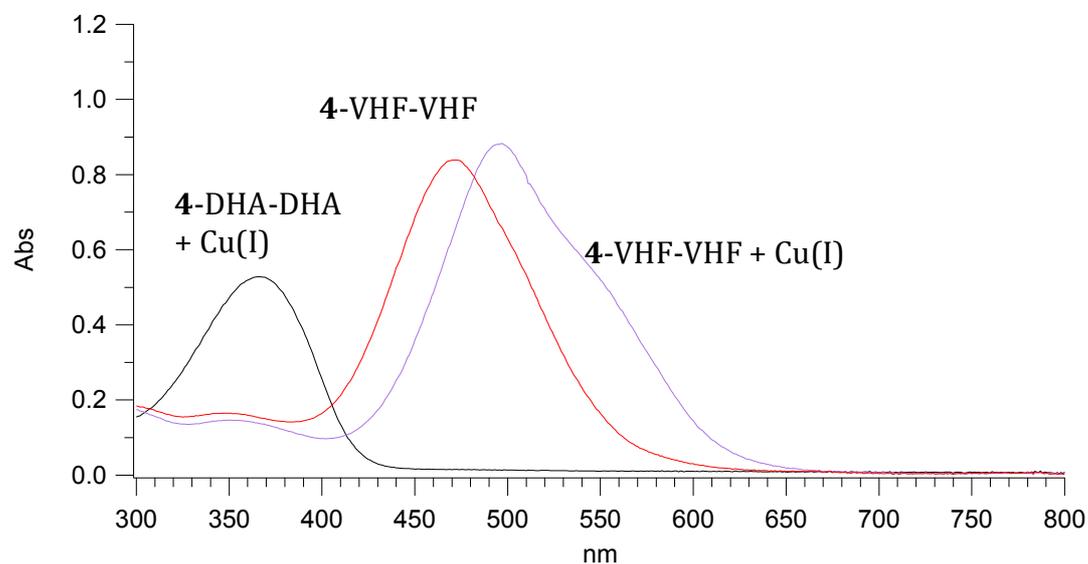
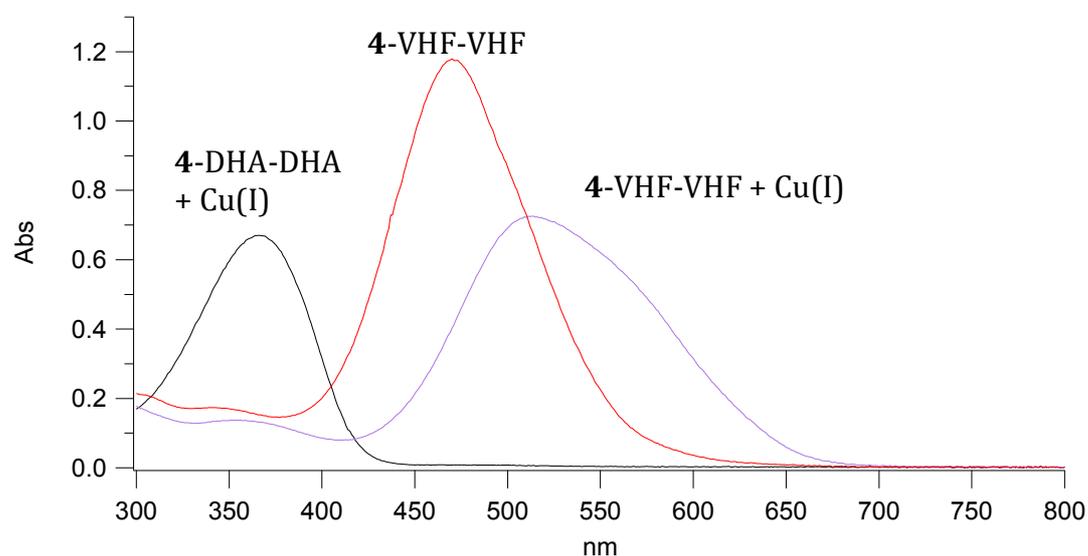
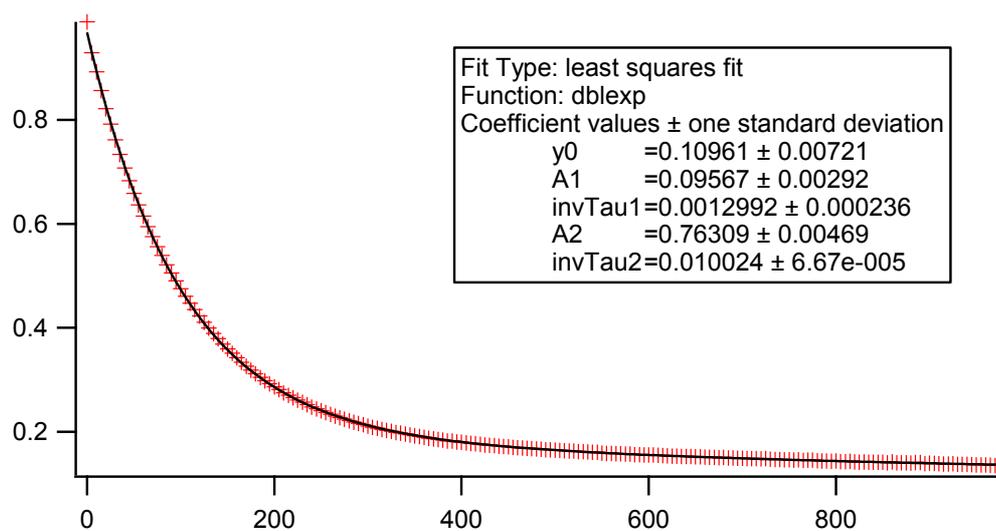
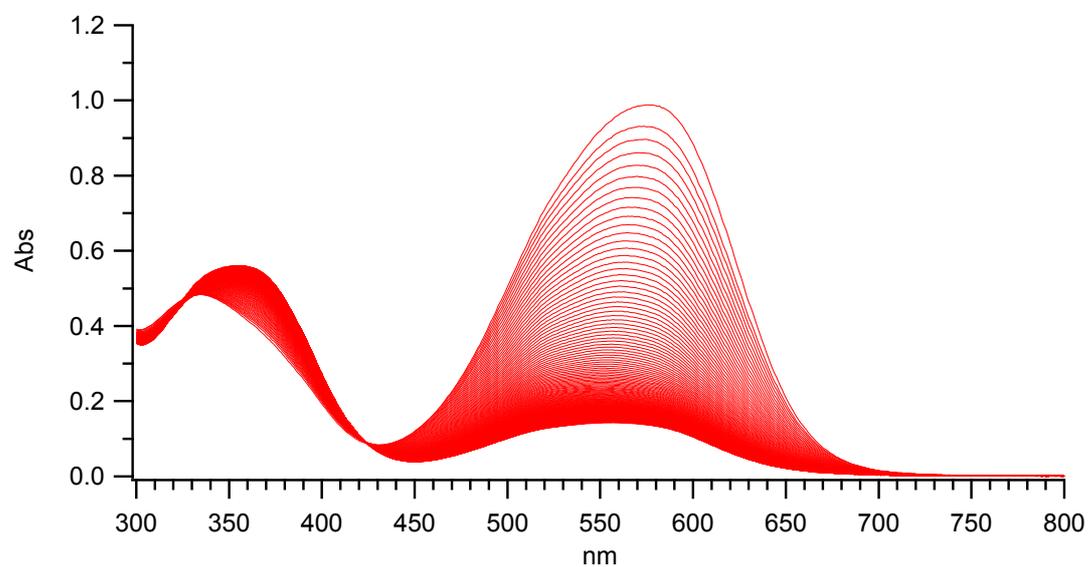


Figure S2. UV-Vis absorption spectra in DCM at 25 °C of **4-DHA-DHA** (black), **4-VHF-VHF** (red), **4-VHF-VHF** after addition 2.7 equiv. per DHA unit of Cu(I) (violet), showing the redshift from 470 nm to 515 nm of the VHF maximum.



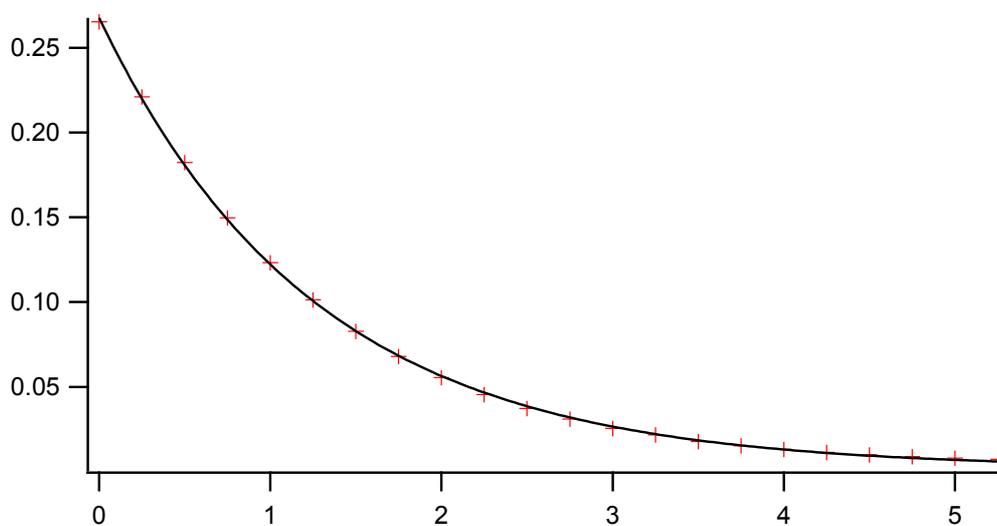
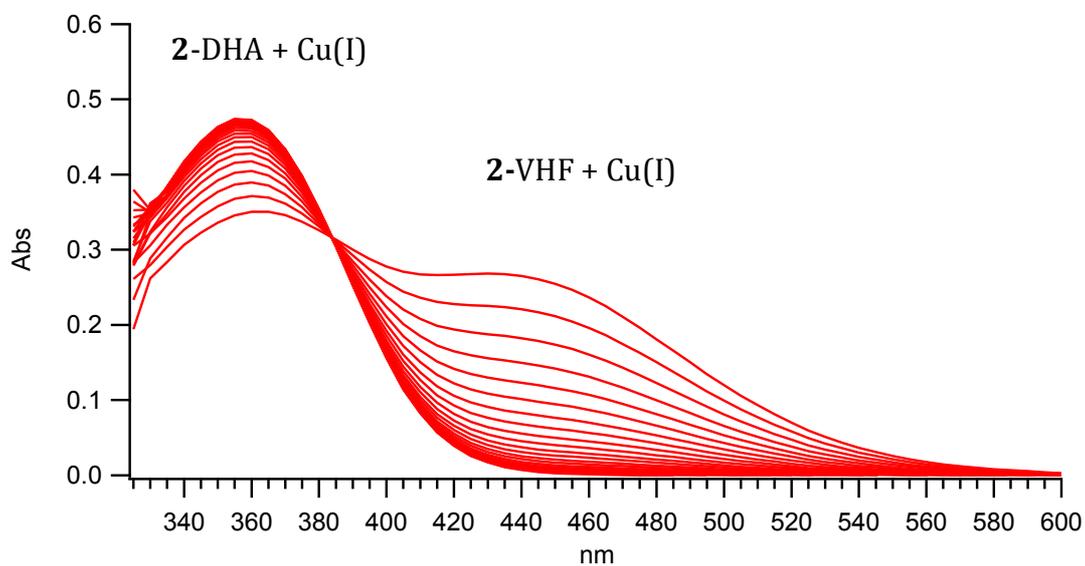
Thermal back reaction of 5-VHF-VHF to 5-DHA-DHA upon addition of **2-3 equiv. of Cu(I) in DCM per DHA unit** at 25 °C and fit of the absorbance at 578 nm with double exponential function

Half-lives: 69 min, 534 min



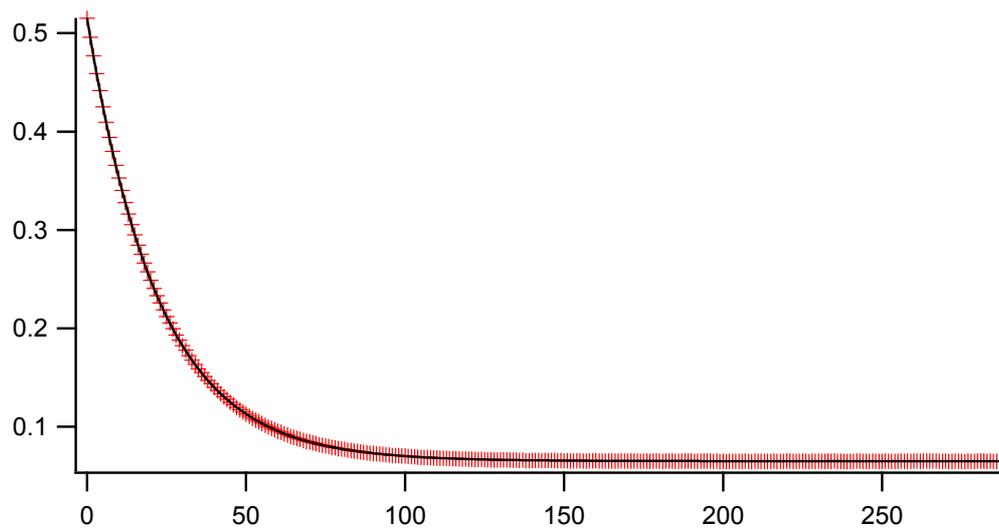
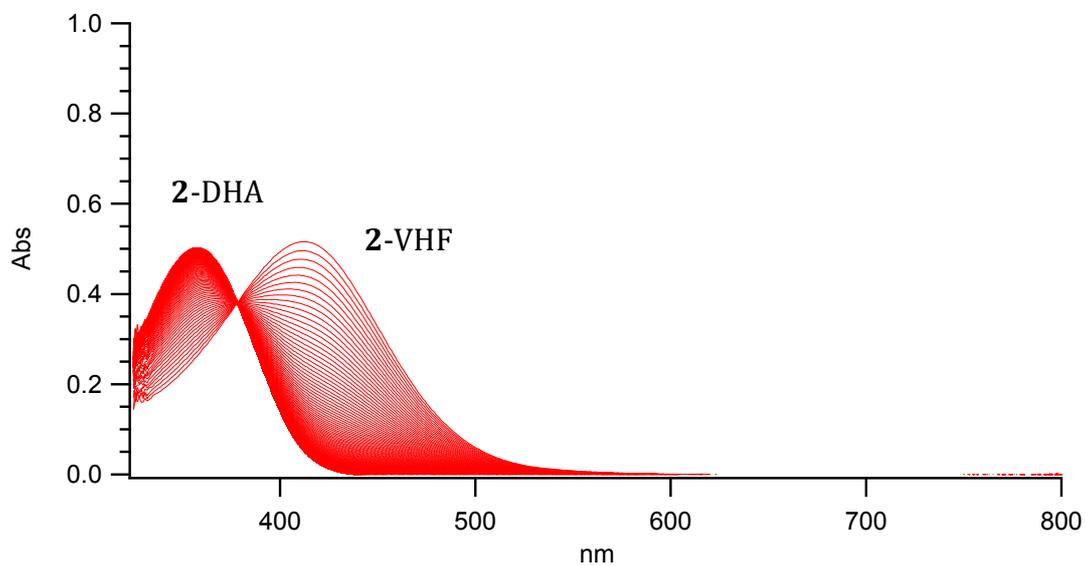
Thermal back reaction of **2-VHF** to **2-DHA** upon addition of **1 equiv. of Cu(I)** (TBR of the complex VHF-Cu(I) to DHA-Cu(I)) in **acetone** at 25 °C and fit of the absorbance at 450 nm.

Half-life: 0.9 min



Thermal back reaction of **2-VHF** to **2-DHA** in **acetone** at 25 °C and fit of the absorbance at 413 nm.

Half-life: 15 min



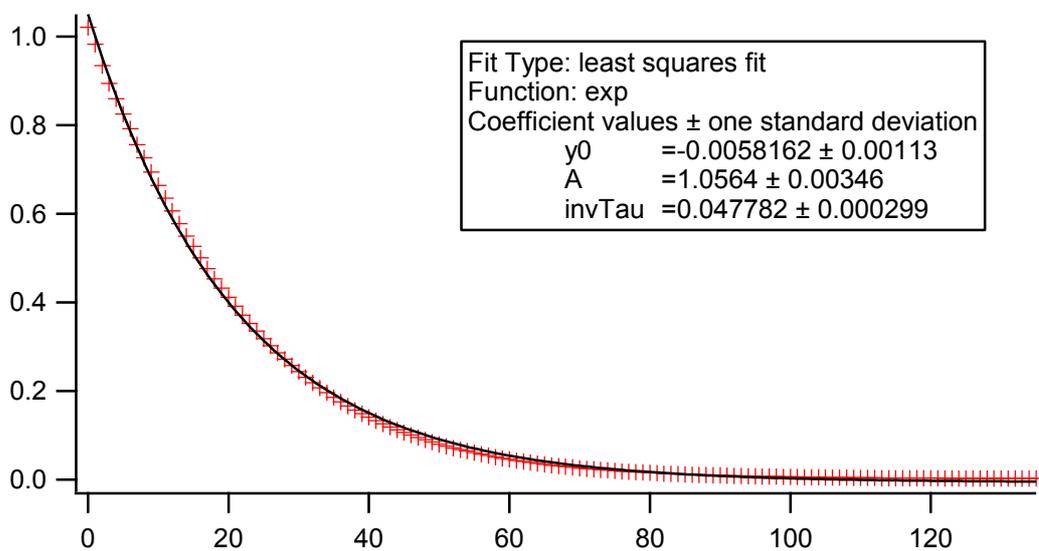
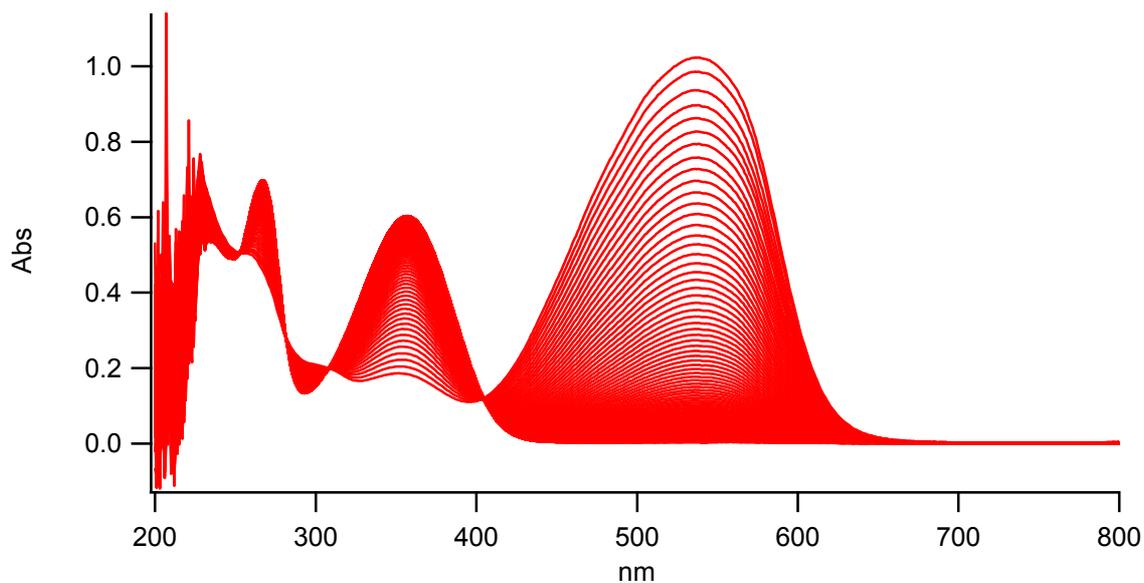
Movie of addition of excess of ethylenediamine to the 5-VHF-VHF + Cu(I) solution:



RECYCLABILITY experiments

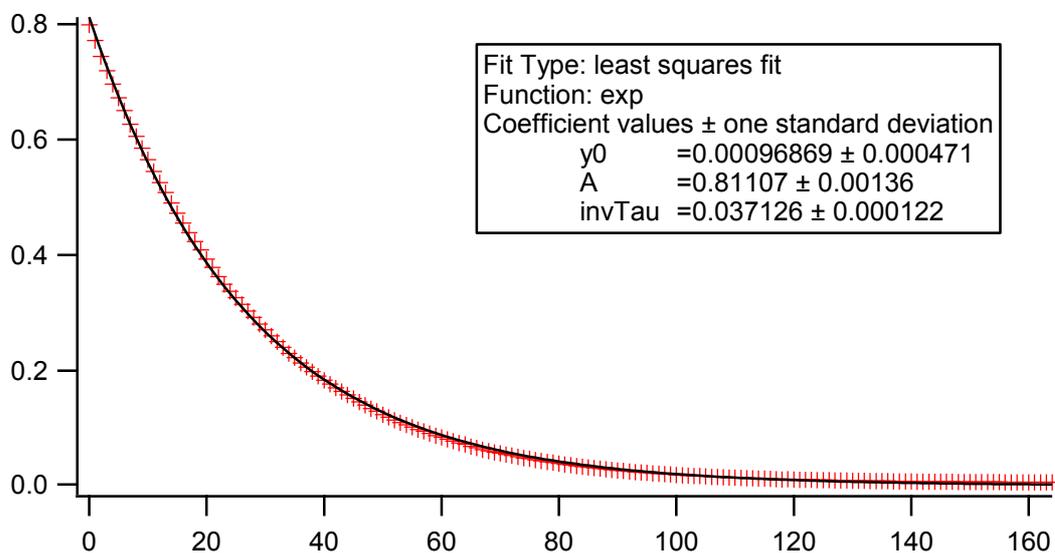
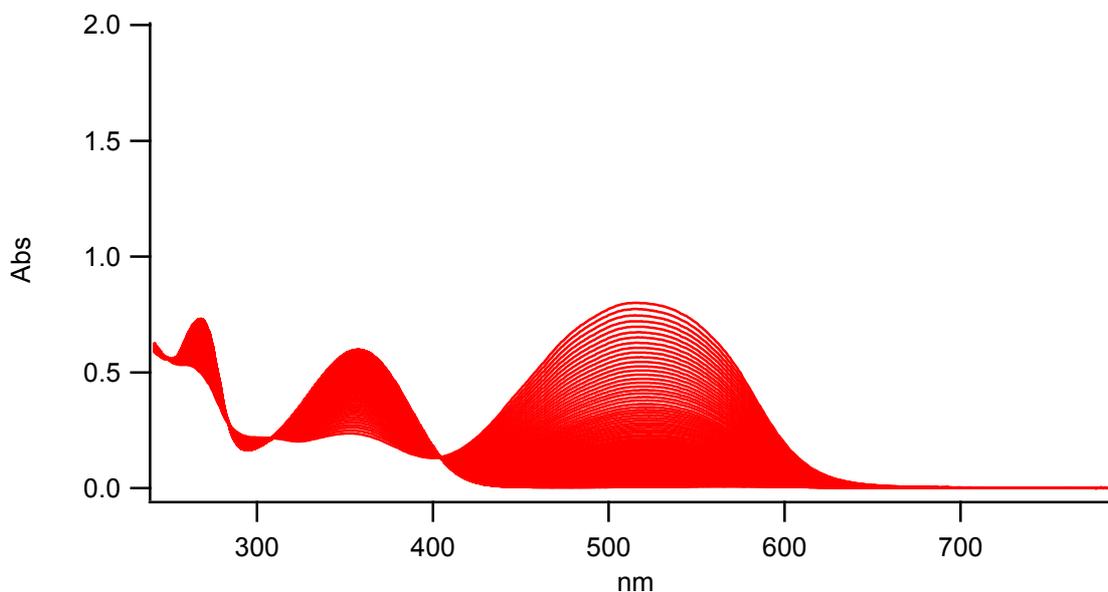
First Cycle: A sample of **1-DHA** in DCM was irradiated for 60 s at 365 nm until full conversion to **1-VHF** was detected by UV, then 1 equiv. of Cu(I) in DCM was added and the thermal back reaction (TBR) of **1-VHF** to **1-DHA** monitored within time at 25 degree (top: TBR 1st cycle, bottom: fit of the Absorbance at 540 nm).

Half-life: 15 min



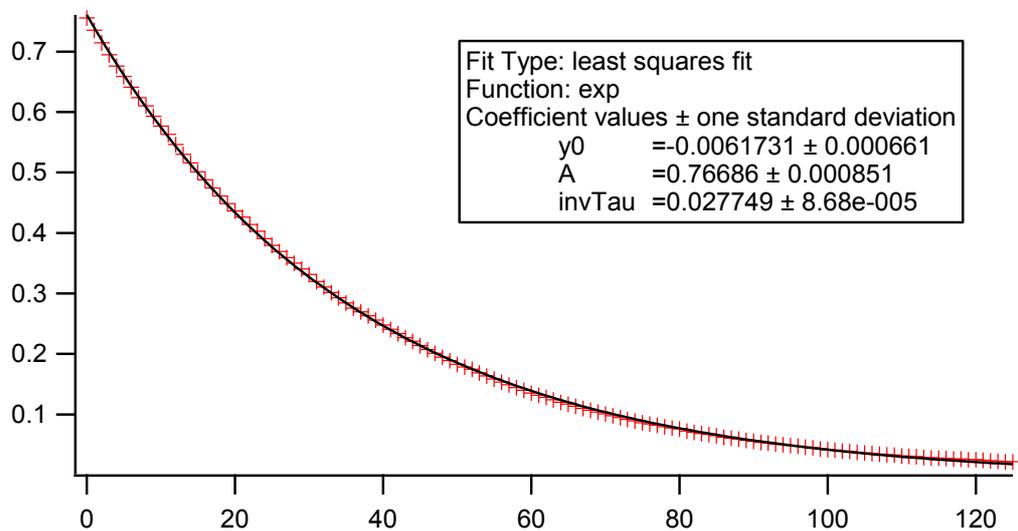
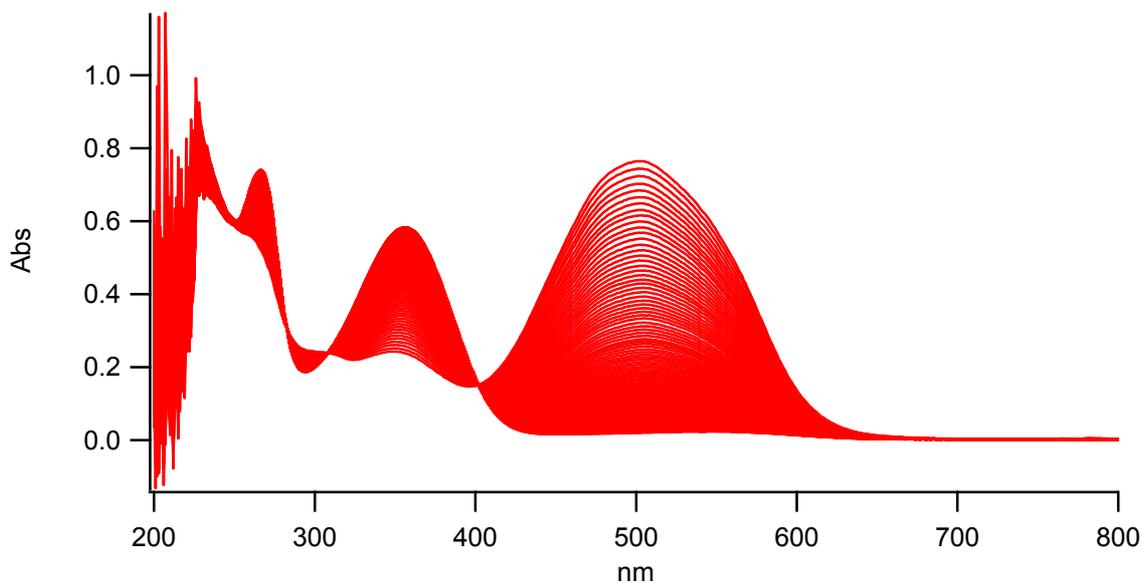
Second Cycle: a stoichiometric amount of ethylenediamine solution in DCM was added to the sample from the first cycle, then the sample was irradiated for 60 s at 365 nm until full conversion to **1-VHF** was detected by UV, then 1 equiv. of Cu(I) in DCM was added and the thermal back reaction (TBR) of **1-VHF** to **1-DHA** monitored within time at 25 degree (top: TBR 2nd cycle, bottom: fit of the Absorbance at 520 nm).

Half-life: 19 min



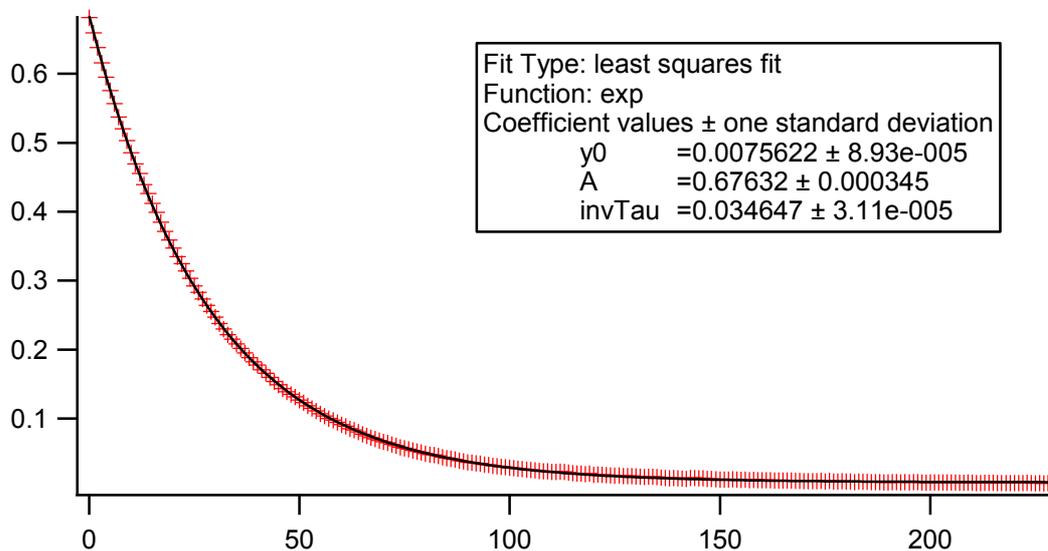
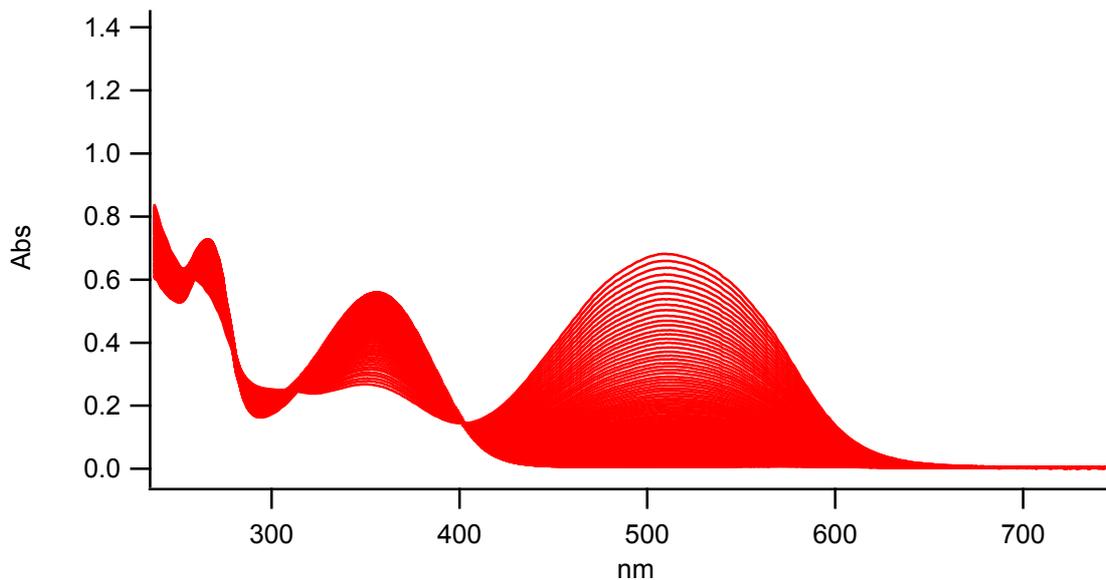
Third Cycle: a stoichiometric amount of ethylenediamine solution in DCM was added to the sample from the second cycle, then the sample was irradiated for 60 s at 365 nm until full conversion to **1-VHF** was detected by UV, then 1 equiv. of Cu(I) in DCM was added and the thermal back reaction (TBR) of **1-VHF** to **1-DHA** monitored within time at 25 degree (top: TBR 3rd cycle, bottom: fit of the Absorbance at 510 nm).

Half-life: 25 min



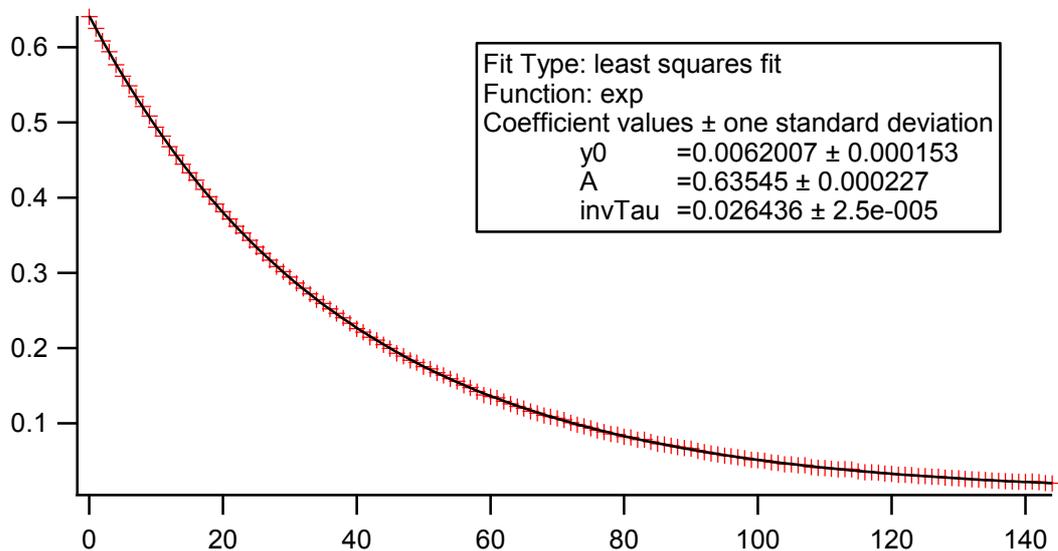
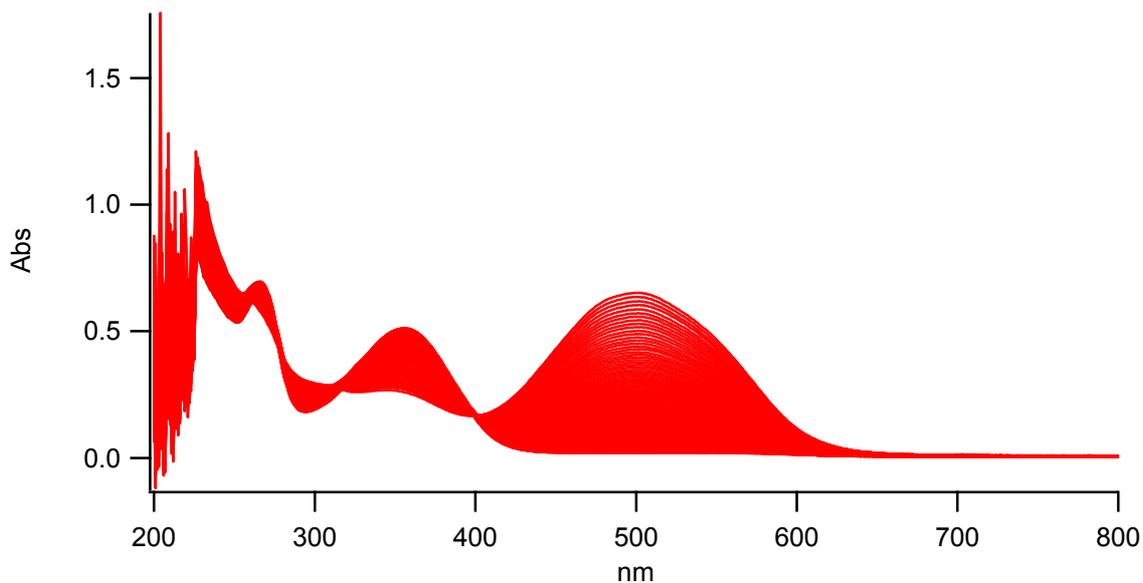
Fourth Cycle: a stoichiometric amount of ethylenediamine solution in DCM was added to the sample from the third cycle, then the sample was irradiated for 60 s at 365 nm until full conversion to **1-VHF** was detected by UV, then 1 equiv. of Cu(I) in DCM was added and the thermal back reaction (TBR) of **1-VHF** to **1-DHA** monitored within time at 25 degree (top: TBR 4th cycle, bottom: fit of the Absorbance at 510 nm).

Half-life: 20 min



Fifth Cycle: a stoichiometric amount of ethylenediamine solution in DCM was added to the sample from the fourth cycle, then the sample was irradiated for 60 s at 365 nm until full conversion to **1-VHF** was detected by UV, then 1 equiv. of Cu(I) in DCM was added and the thermal back reaction (TBR) of **1-VHF** to **1-DHA** monitored within time at 25 degree (top: TBR 5th cycle, bottom: fit of the Absorbance at 510 nm).

Half-life: 26 min



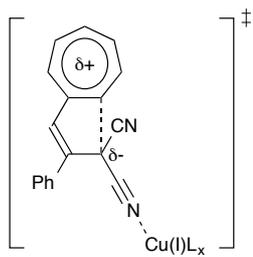


Figure S1. The polarized VHF-to-DHA TS structure is likely stabilized by complexation of Cu(I). L = ligand.