Supporting Information to

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Synthesis

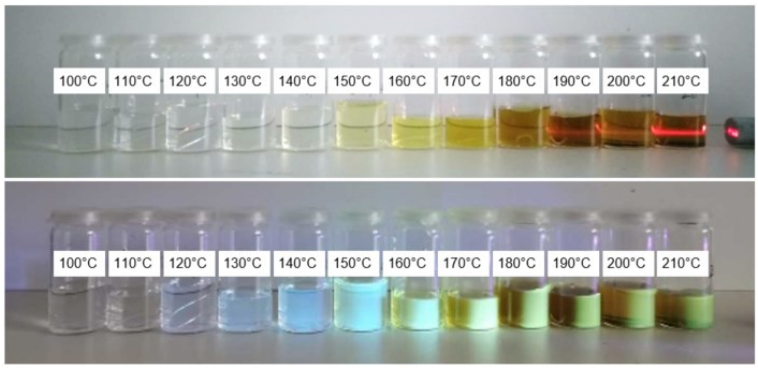


Figure S1. *Photograph of aqueous sample solutions of the crude products (conc: 0.2 mg/mL) synthesized at temperatures between 100 – 220°C under illumination with a red laser (top) and under illumination with a UV-lamp (365 nm) (bottom).*

Nuclear Magnetic Resonance Spectroscopy of the Raw Products

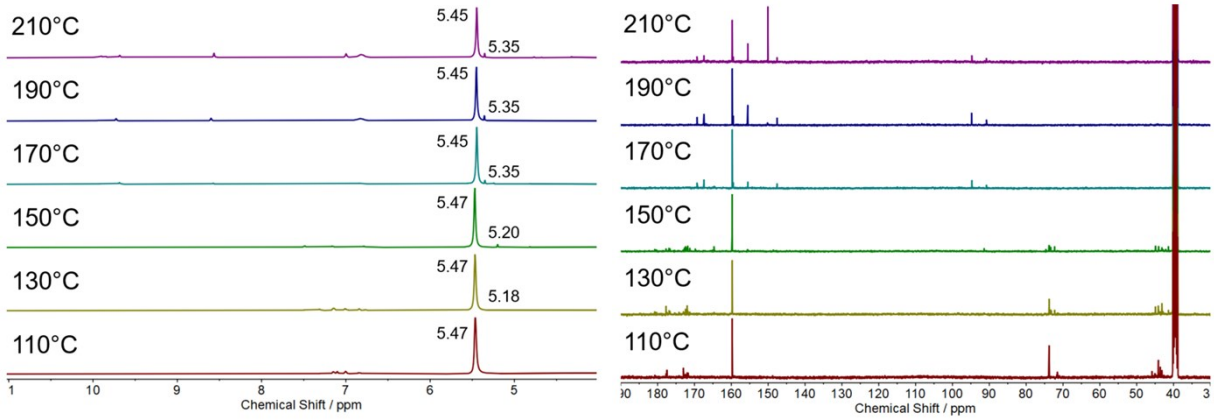


Figure S2. *^{1}H-NMR (left) and ^{13}C-NMR (right) spectra of selected raw products of the CA/U reaction at different temperatures between 110-210°C.*

UV-vis and Fluorescence Spectroscopy of the Raw Products

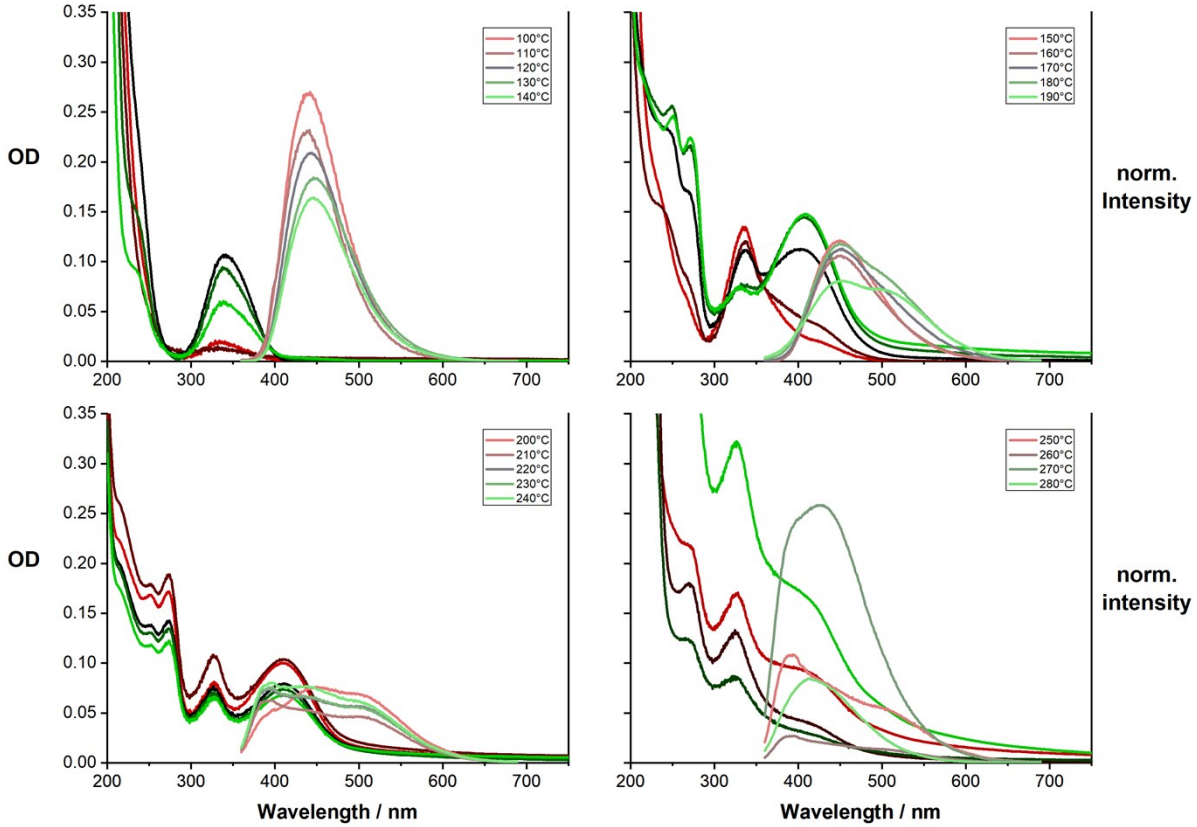


Figure S3. *Combined electronic absorption (red to green) and excitation normalized (λ_{ex} = 350 nm) emission (pale red to pale green) spectra of crude CA/U products (0.013 mg/mL) synthesized at different temperatures between 100 – 290°C; a) 100 – 140°C; b) 150 – 190°C; a) 200 – 240°C; a) 250 – 290°C.*

Nuclear Magnetic Resonance Spectroscopy of the Educts and References

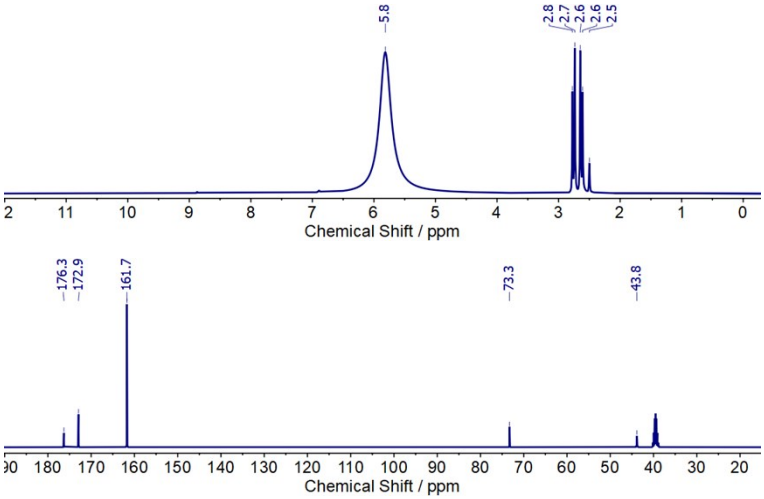


Figure S4. *Top: [1]H-NMR (top) and [13]C-NMR (bottom) spectra of* ***citric acid*** *and* ***urea*** *in DMSO-d6.*

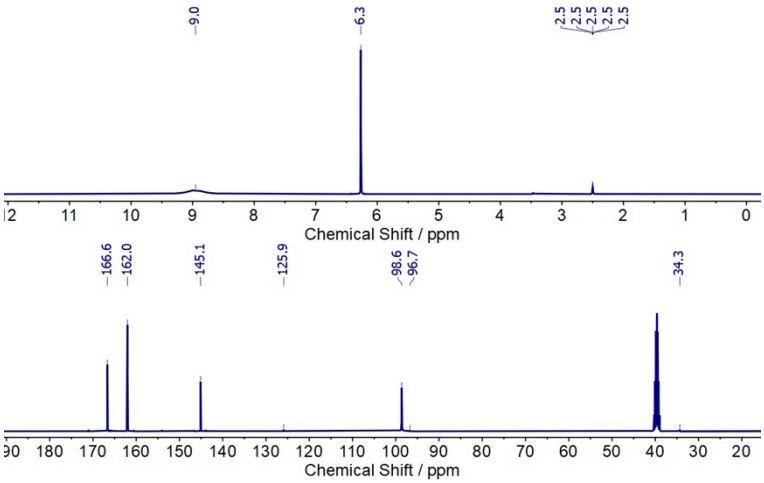


Figure S5. *Top: [1]H-NMR (top) and [13]C-NMR (bottom) spectra of* ***citrazinic acid*** *(commercial) in DMSO-d6.*

Separation of the Raw Products

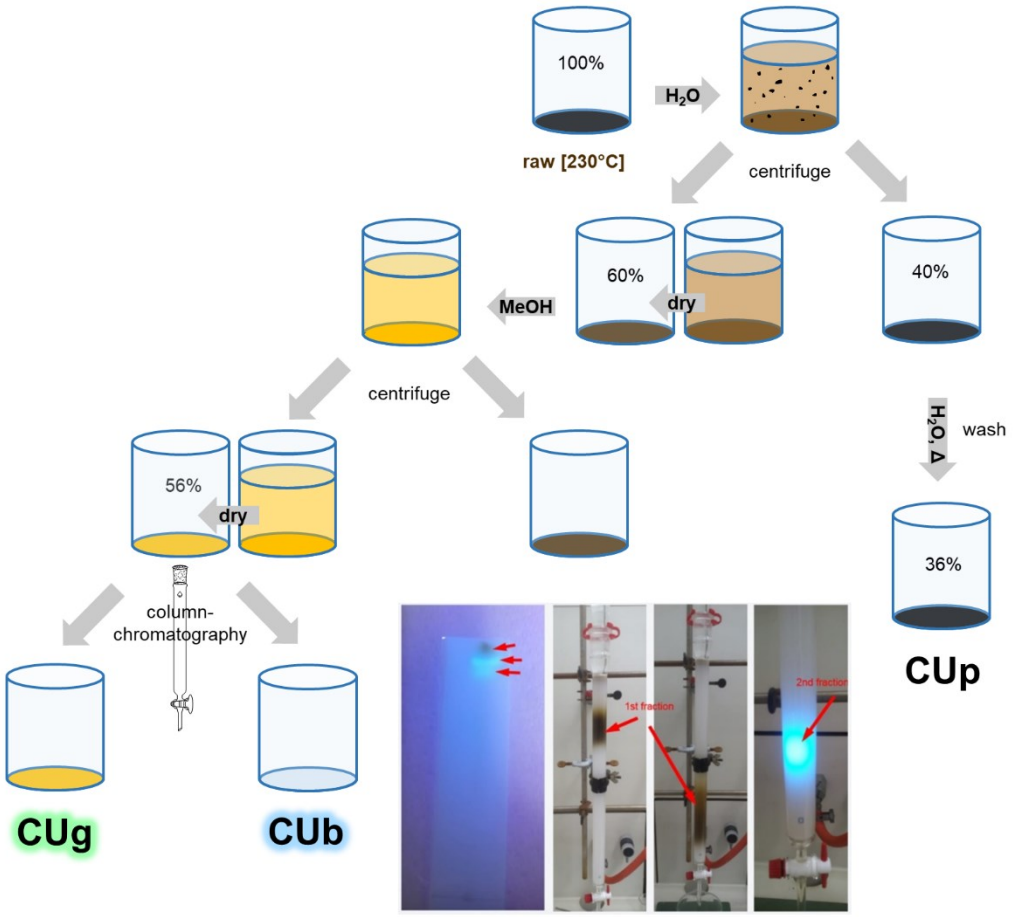


Figure S6. *Illustration of the separation process of the raw products obtained from a thermal CA/U reaction.*

Extinction coefficients of CUg

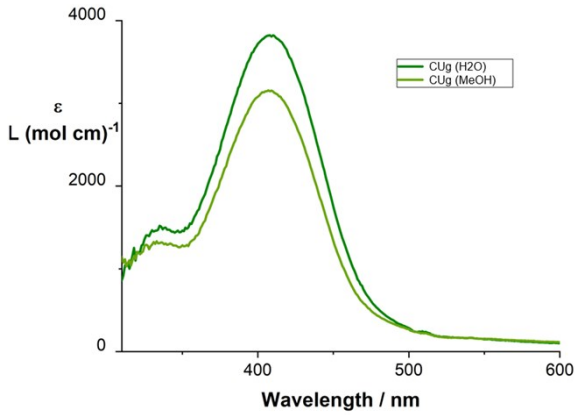


Figure S7. *Molar extinction coefficients of* ***CUg*** *in H_2O and MeOH.*

Time-correlated Single-Photon Counting of CUg and CUb

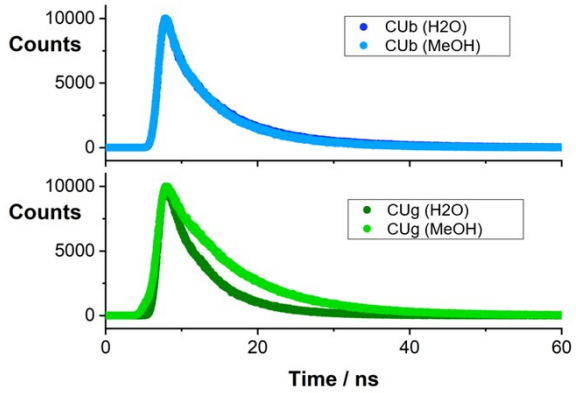


Figure S8. *Fluorescence lifetime decay profiles obtained by TCSPC of* ***CUb*** *and* ***CUg*** *in H_2O and MeOH at room temperature obtained upon excitation at 370 or 450 nm, respectively .*

Table S1. *Fluorescence lifetimes of* ***CUb*** *and* ***CUg*** *in MeOH and H_2O.*

		τ_1 ns	A_1 %	τ_2 ns	A_2 %
CUb	MeOH	3.1	28	7.6	72
	H_2O	4.1	45	9.5	55
CUg	MeOH	9.0	100		
	H_2O	5.3	100		

Fluorescence Quantum Yields of CUg

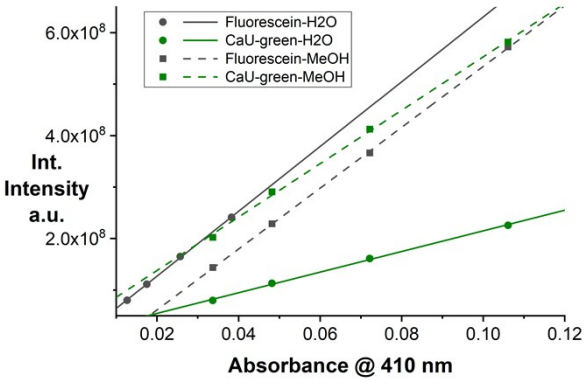


Figure S9. *Determination of the fluorescence quantum yields of* ***CUg*** *in H_2O and MeOH using Na-fluorescein as a standard.*

Table S2. *Fluorescence quantum yields of* ***CUg*** *determined by the gradient method using Na-fluorescein as a standard and in MeOH and H_2O.*

	solvent	slope	φ_{Fl} (%)
Na-Fluorescein	H_2O	6.30E+09	**85**[64]
	MeOH	5.90E+09	**79**
CUg	H_2O	2.00E+09	**27**
	MeOH	5.20E+09	**70**

Photostability of CUg

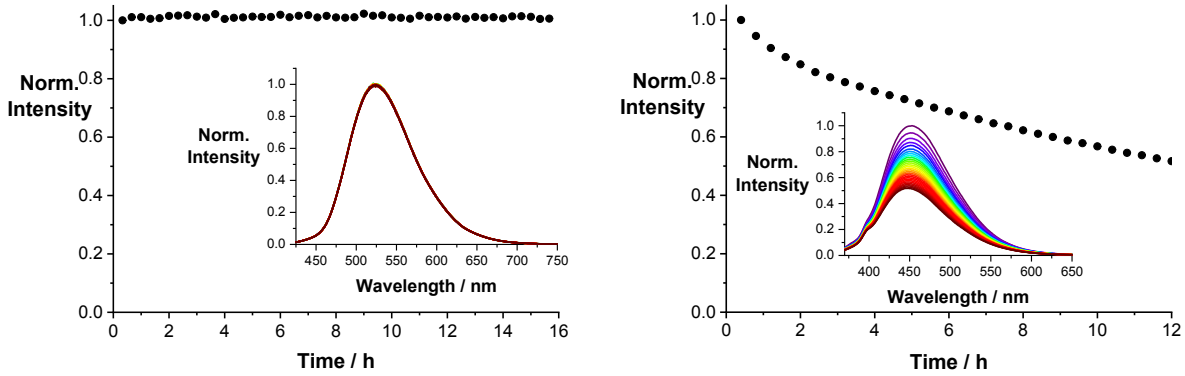


Figure S10. *Left: photo-stability measurement of a 8.3×10^{-5} M solution of* ***CUg*** *in H_2O. The sample was constantly illuminated for 16h. The inset shows the fluorescence spectra in time intervals of 20 min; Right: Photo-stability measurement of* ***CUb*** *in H_2O. The inset shows the fluorescence spectra in time intervals of 24 min from purple to red.*

ESI - mass spectrometry of CUg and CUb

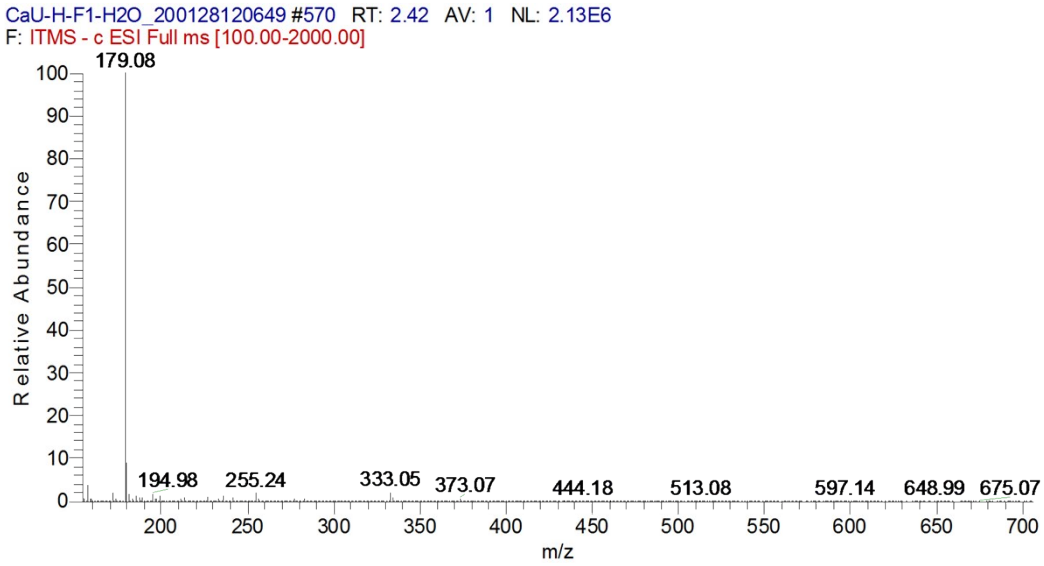


Figure S11. *Liquid chromatography-electrospray ionization - mass spectrum of* ***CUg*** *obtained in negative ion mode.*

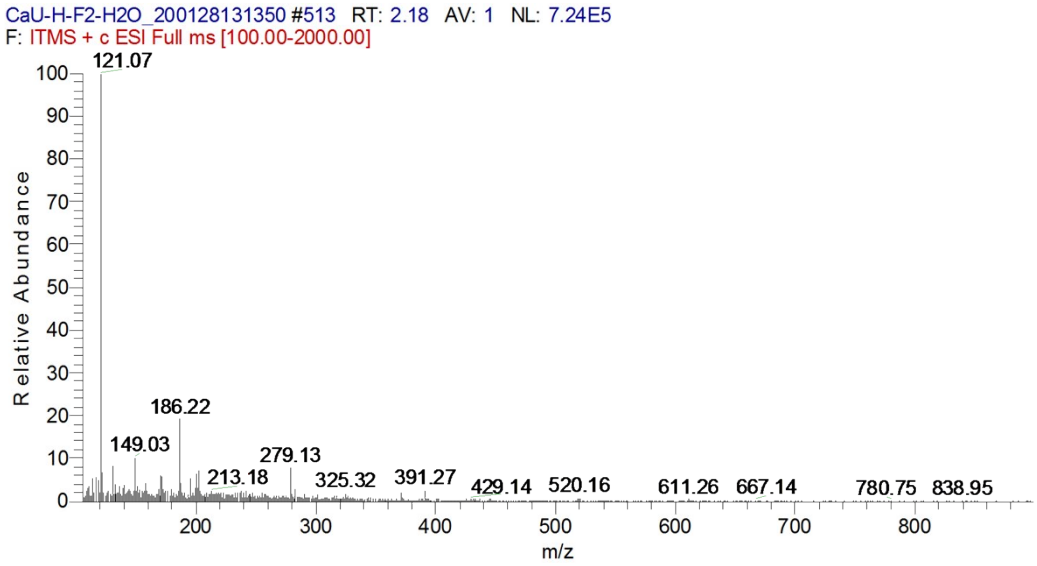


Figure S12. *Liquid chromatography – electrospray ionization - mass spectrum of* ***CUb*** *obtained in positive ion mode.*

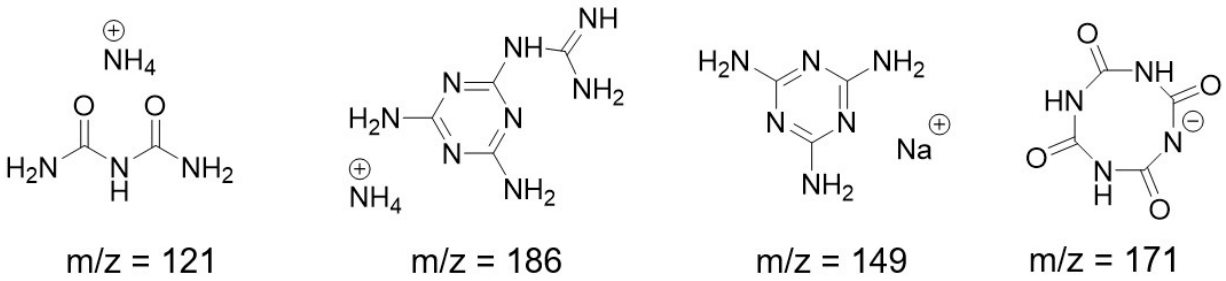


Figure S13. *Potential compounds detected in the ESI-mass spectra of CUb.*

2D-Correlation NMR of CUg

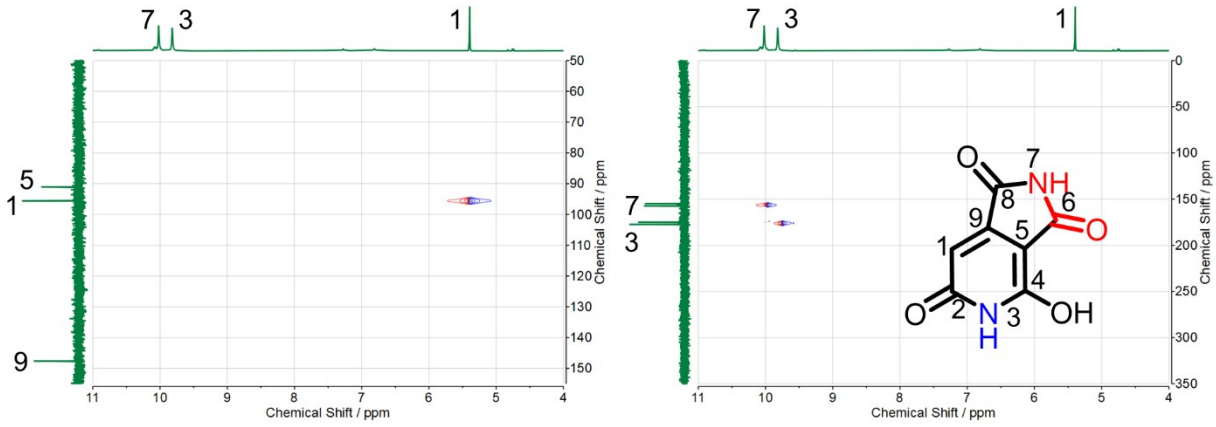


Figure S14. *HSQC-C (left) and HSQC-N (right) of* ***CUg*** *in DMSO-d6 showing the direct coupling of* ^{1}H *to* ^{13}C *or* ^{15}N*, respectively.*

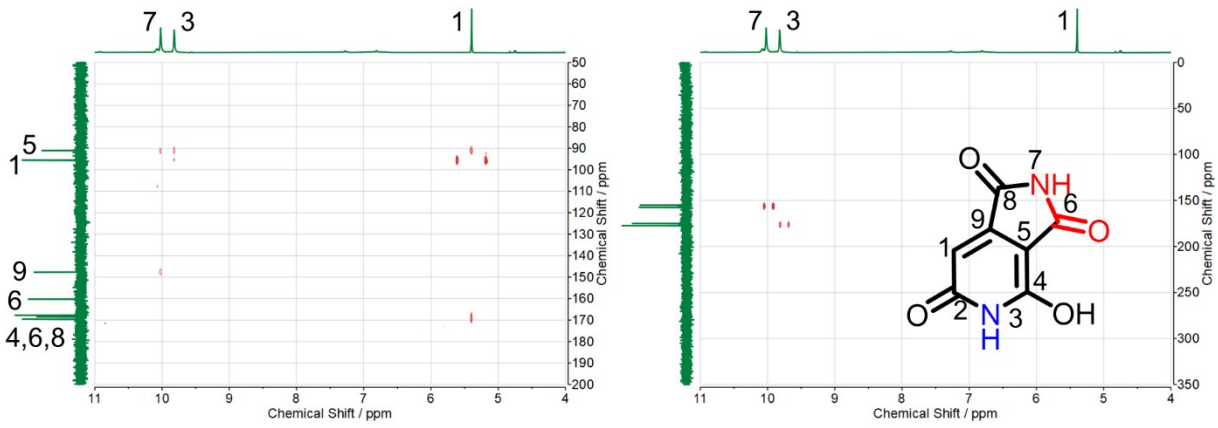


Figure S15. *HMBC-C (left) and HMBC-N (right)* ***CUg*** *enriched with ^{15}N in DMSO-d6 showing the three-bond coupling of ^{1}H to ^{13}C or ^{15}N, respectively.*

DFT calculations of CUg (HPPT)

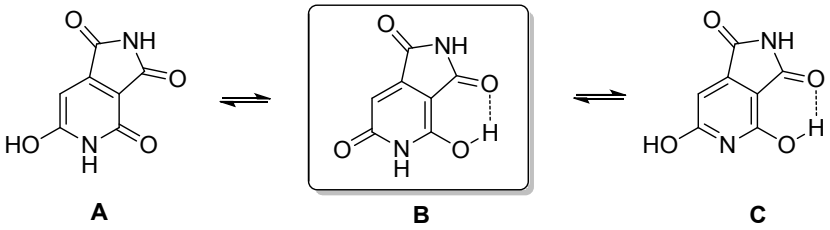
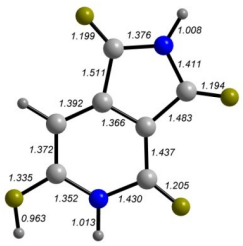
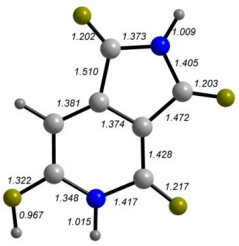
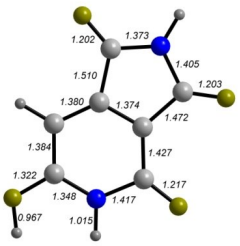
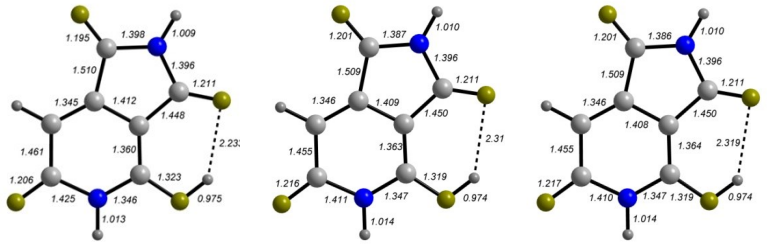
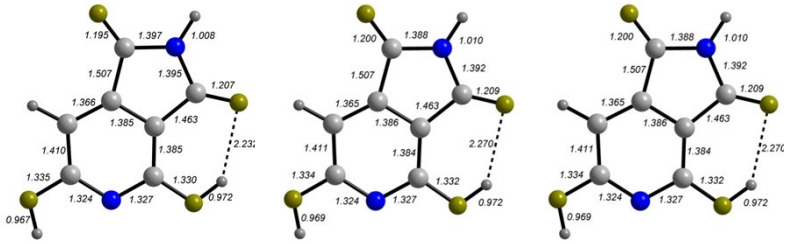


Figure S16*. Molecular structures of the tautomeric forms of HPPT.*

Table S3. *DFT calculated tautomeric forms of HPPT with relative energy values in arbitrary units using M06-2X-D3/def2-TZVP, SCRF: PCM.*

	Geometry (vacuum)	Geometry (MeOH)	Geometry (H_2O)	E_{REL} (vac.)	E_{REL} (MeOH)	E_{REL} (H_2O)
A				+10.9	+ 4.4	+ 4.2

B		**± 0**	**± 0**	**± 0**
C		-0.4	+ 1.6	+ 1.6

2D-Correlation NMR of CUb

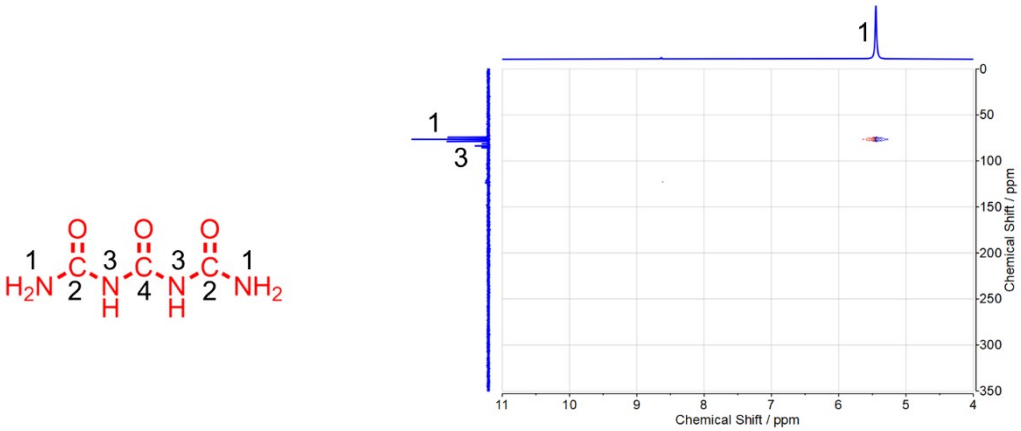


Figure S17. *HSQC-N of* ***CUb*** *enriched with* ^{15}N *in DMSO-d6 showing the direct coupling of* ^{1}H *to* ^{13}C *or* ^{15}N*, respectively.*

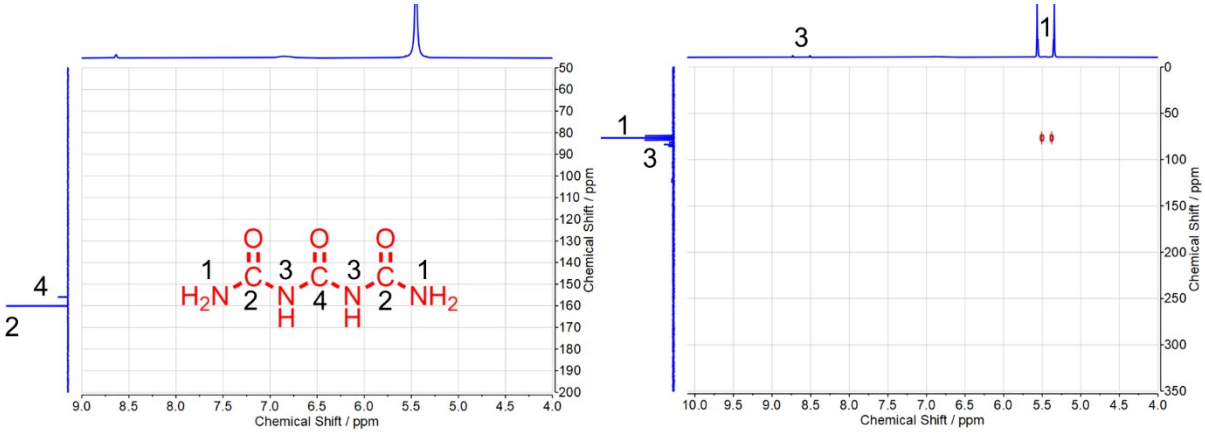


Figure S18. *HMBC-C (left) and HMBC-N (right) of* ***CUb*** *enriched with ^{15}N in DMSO-d6 showing the three-bond coupling of ^{1}H to ^{13}C or ^{15}N, respectively.*

Nuclear Magnetic Resonance Spectroscopy of Biuret

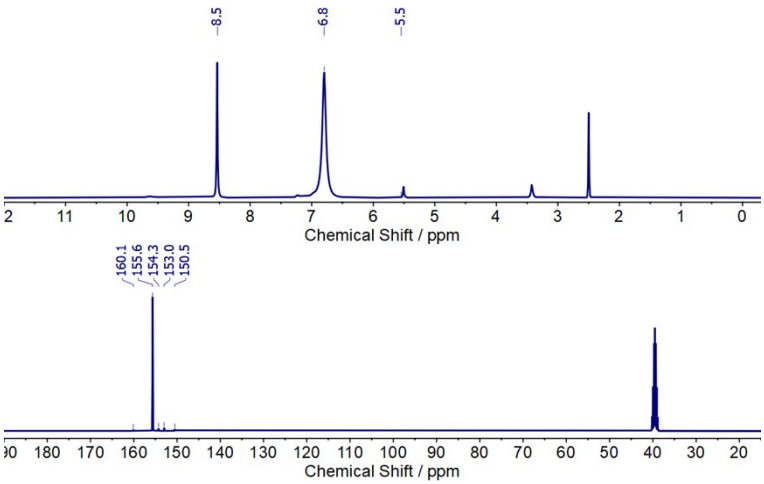


Figure S19. *Top: ^{1}H-NMR (top) and ^{13}C-NMR (bottom) spectra of* ***biuret*** *(commercial) in DMSO-d6.*

Biuret test with CUb

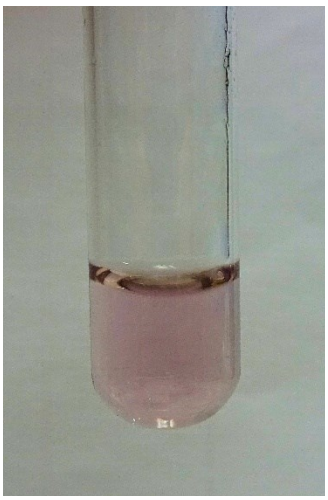


Figure S20. *Photograph of a basic solution of* ***CUb*** *upon addition of a $CuSO_4$ solution.*

Thermal Mass analysis of CUg and CUb

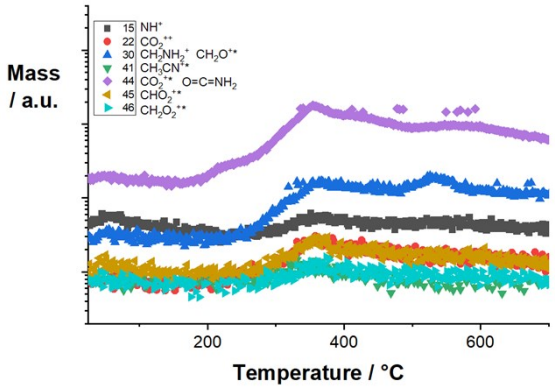


Figure S21. *Temperature dependent mass spectrometric analysis of* ***CUg****.*

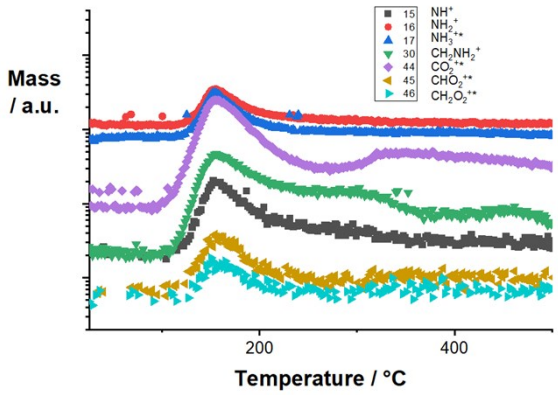


Figure S22. *Temperature dependent mass spectrometric analysis of* ***CUb****.*

Thermogravimetric Analysis of the Raw Mixture

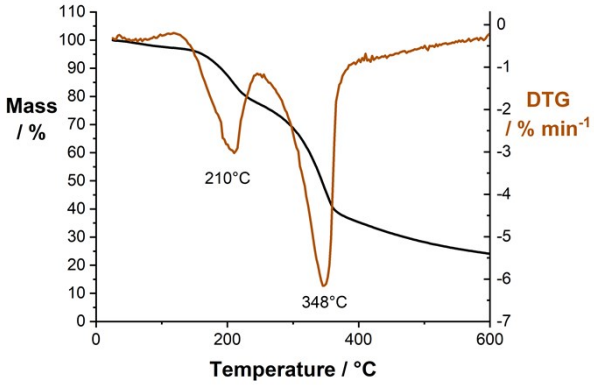


Figure S23. *Thermogravimetric analysis of the supernatant of the raw product before column chromatography containing* ***CUg*** *and* ***CUb.***

X-ray Photoelectron Spectroscopy of CUb and CUg

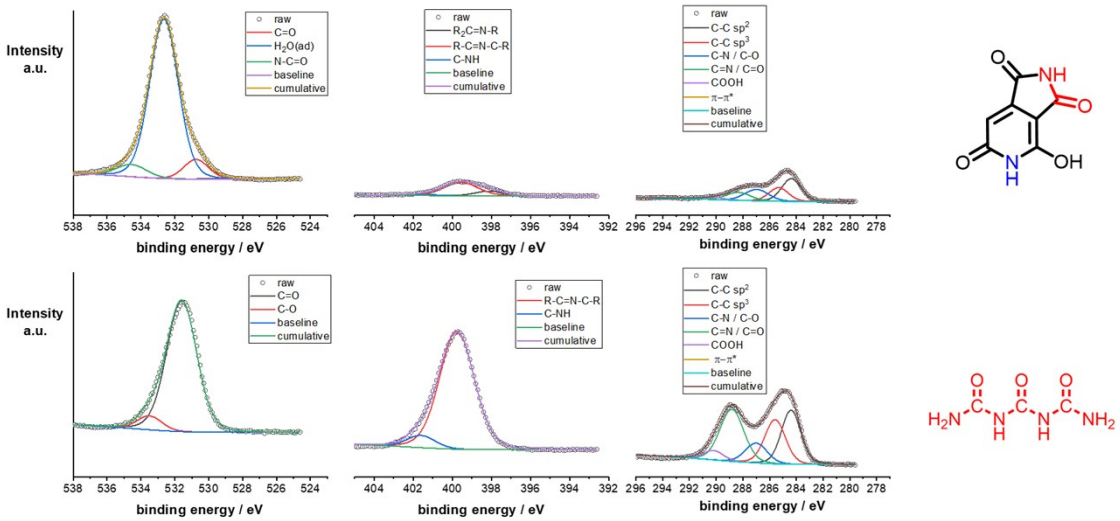


Figure S24. *X-ray photoelectron spectra of* ***CUg*** *(top) and* ***CUb*** *(bottom) with emphasis on the C_{1s}, N_{1s}, and O_{1s} regions.*

Nuclear Magnetic Resonance Spectroscopy during Washing of CUp

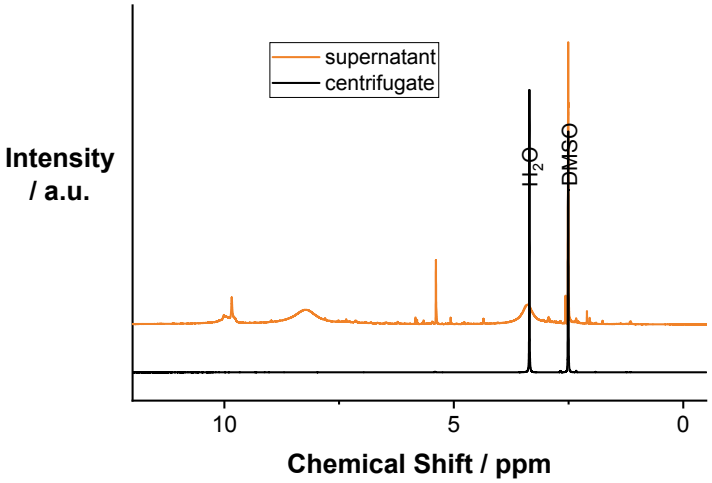


Figure S25. *^{1}H-NMR spectra of the supernatant and the redispersed centrifugate after washing* ***CUp*** *in H_2O at 95°C in DMSO-d6.*

Optical Spectroscopy of dispersions of CUp in H_2O.

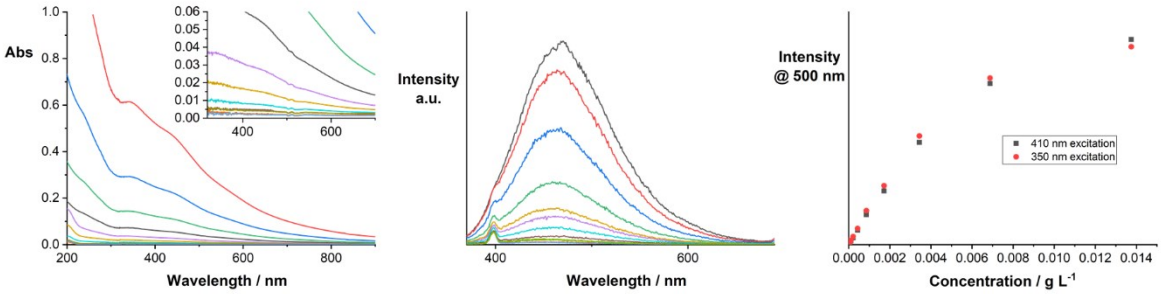


Figure S26. *Absorption (left) and fluorescence (center) spectra of* ***CUp*** *in H_2O at room temperature at different concentrations. Right: Fluorescence intensity versus concentration of* ***CUp*** *in H_2O.*

Nuclear Magnetic Resonance Spectroscopy of a Non-Separated Mixture

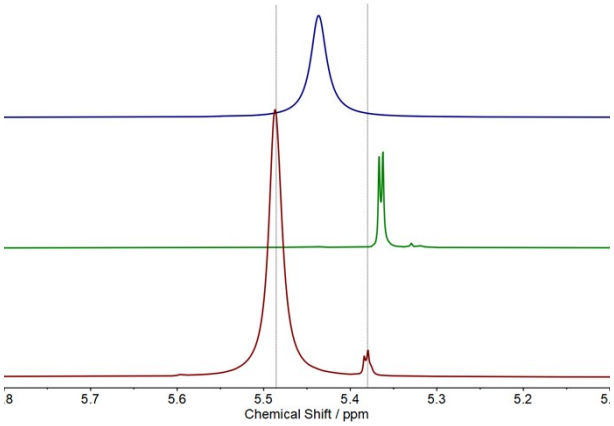


Figure S27. *[1]H-NMR spectra of* ***CUb*** *(top),* ***CUg*** *(center) and the non-separated mixture of* ***CUb*** *and* ***CUg*** *(bottom) in DMSO-d6.*

References (continued from paper)

64. X.-F. Zhang, J. Zhang and L. Liu, Fluorescence Properties of Twenty Fluorescein Derivatives: Lifetime, Quantum Yield, Absorption and Emission Spectra, *J. Fluoresc.*, 2014, **24** (3), 819–826, 10.1007/s10895-014-1356-5