Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Tetraguanidino-Functionalized Phenazine and Fluorene Dyes: Synthesis and Coordination Chemistry

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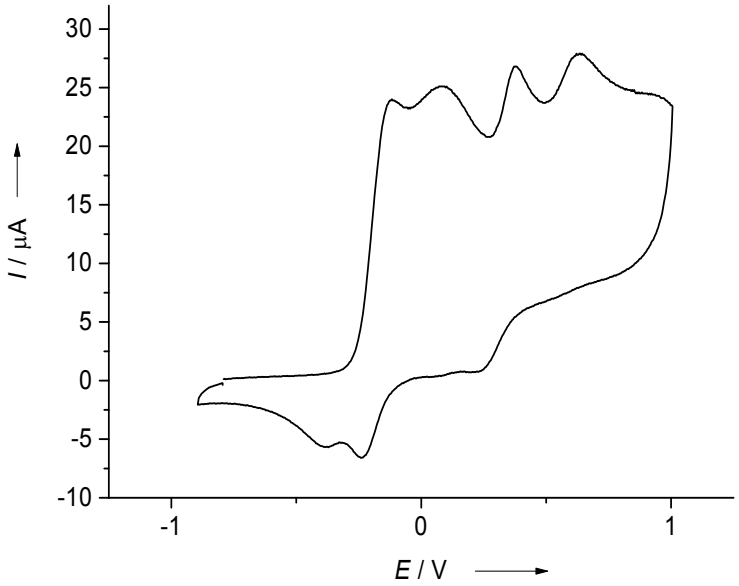
Figure S1. a) CV curve recorded for **1** (CH_2Cl_2, c = 10^{-3} mol/l, Ag/AgCl electrode, potentials relative to Fc/Fc^+ (Fc = ferrocene), [(*n*-Bu)$_4$N][PF_6], c = 0.1 mol/l).



b) CV curve recorded for **1** (CH_2Cl_2, c = 10^{-3} mol/l, Pt electrode, potentials relative to Fc/Fc^+ (Fc = ferrocene), [(*n*-Bu)$_4$N][PF_6], c = 0.1 mol/l).

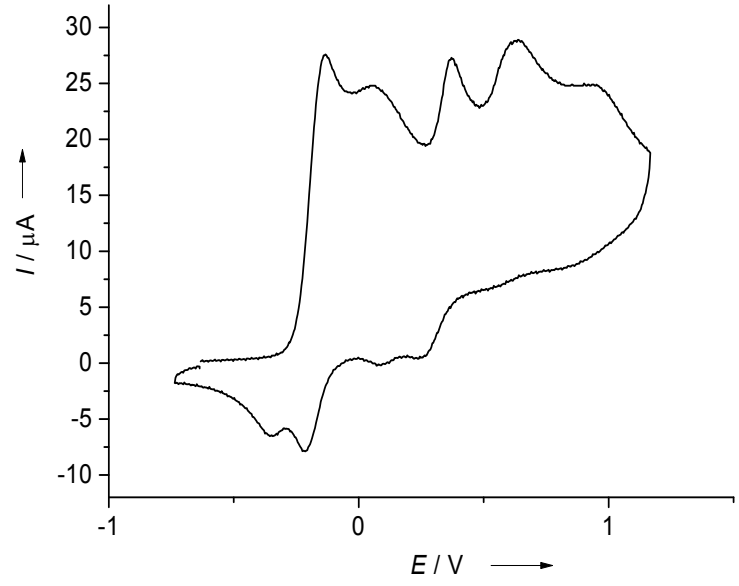
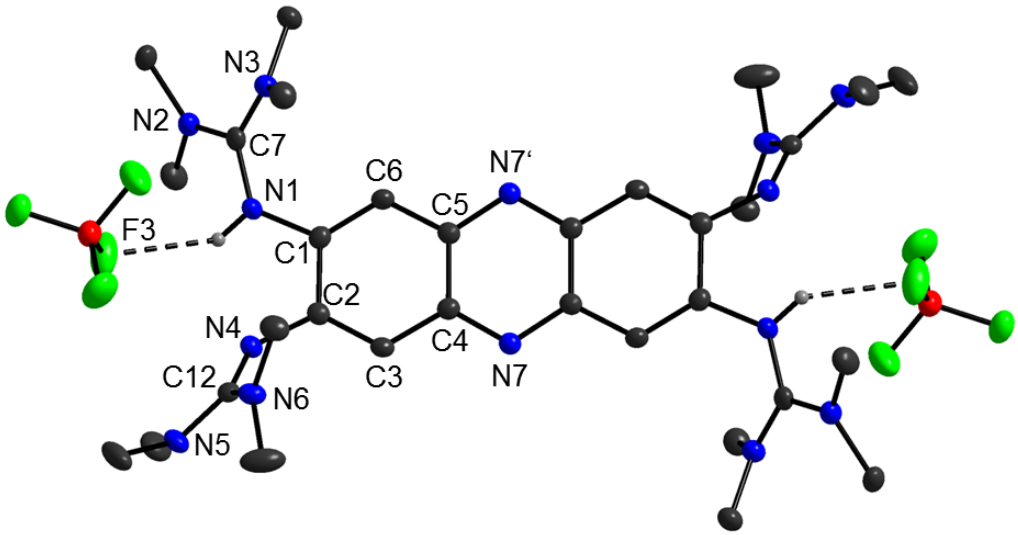


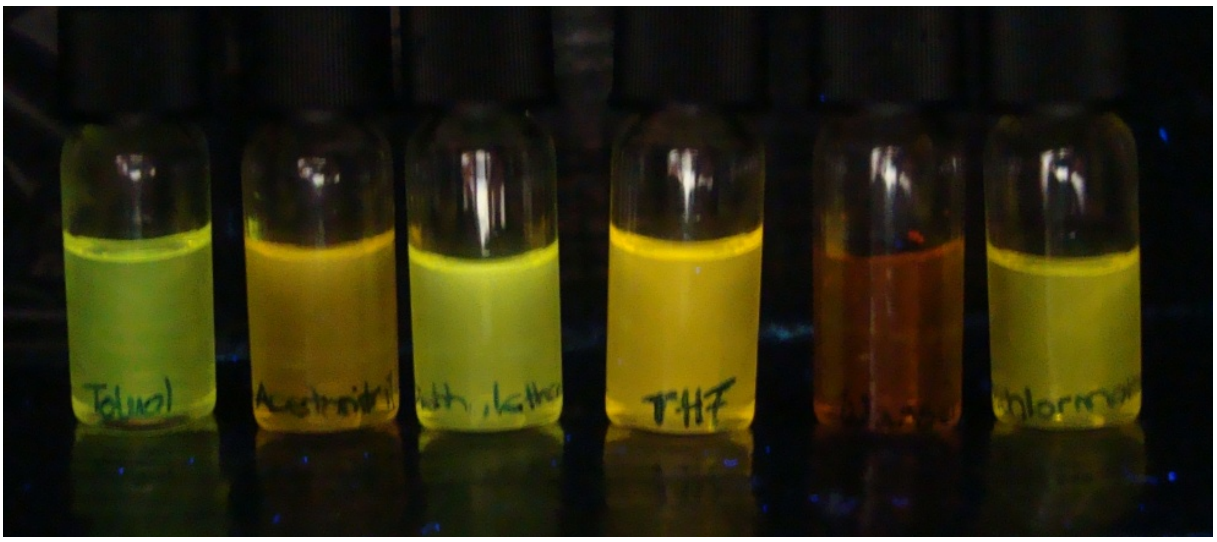
Figure S2. c) Structure of [**1**H_2](BF_4)$_2$. Vibrational ellipsoids drawn at the 50% probability level. Hydrogen atoms omitted for sake of clarity. Selected bond distances (in Å): N1-C1 1.4001(18), N1-C7 1.3545(19), N2-C7 1.3253(19), N3-C7 1.3401(19), N4-C2 1.3874(18), N4-C12 1.3055(19), N5-C12 1.3672(19), N6-C12 1.3684(19), C1-C2 1.451(2), C1-C6 1.360(2), C2-C3 1.373(2), C3-C4 1.417(2), C4-N7 1.3476(18), C4-C5 1.4362(19), C5-N7' 1.3433(18), C5-C6 1.422(2), N1H-F3 2.338.



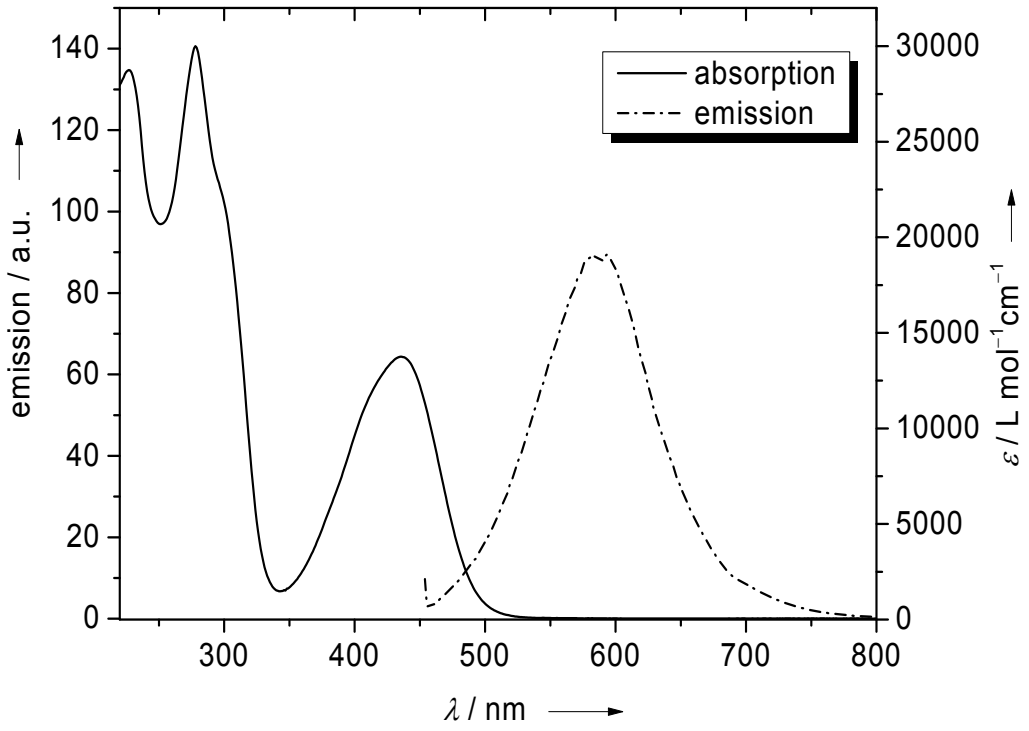
Crystal data for [**1**H_2](BF_4)$_2$, $C_{32}H_{54}B_2F_8N_{14}$: *M*r = 808.51, 0.0850 x 0.0680 x 0.0298 mm^3, monoclinic, space group $P2_1/n$, a = 8.10458(13), b = 30.8148(4), c = 8.16009(13) Å, β = 94.0820(16)°, V = 2032.74(6) Å^3, Z = 2, d_{calc} = 1.321 Mg·m^{-3}, Mo $K\alpha$ radiation (graphite monochromated, λ = 0.71073 Å), T = 100 K, θ_{range} 2.811 to 35.250°. Reflections measd. 57051, indep. 3867, R_{int} = 0.0495. Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0374, wR_2 = 0.0941.

Figure S3. a) Photos showing the emission of solutions of compound **5** in different organic solvents under UV-light (from left to right: toluene, CH_3CN, Et_2O, THF, H_2O and CH_2Cl_2). b) Electronic absorption and emission spectra for solutions of compound **5** in THF solution. c) Electronic absorption and emission spectra for solutions of compound **5** in Et_2O solution.

a)



b)



c)

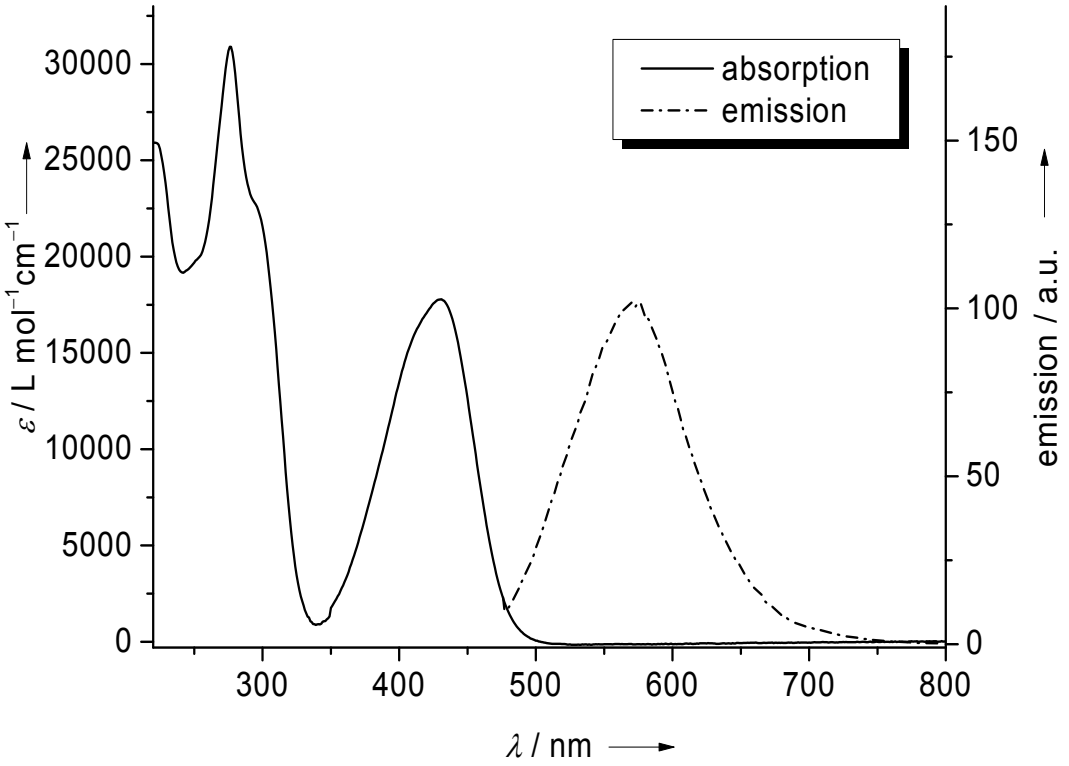
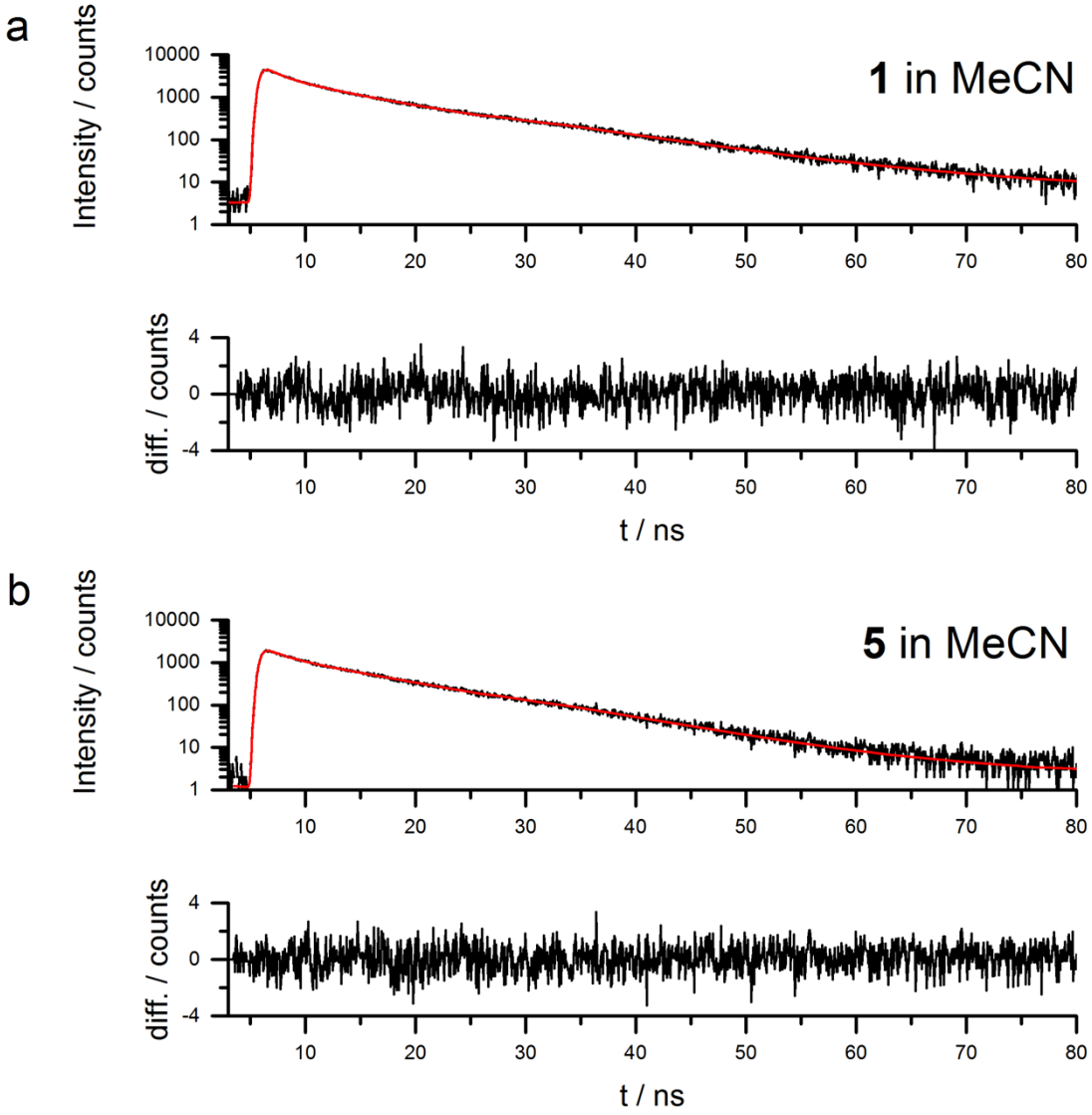
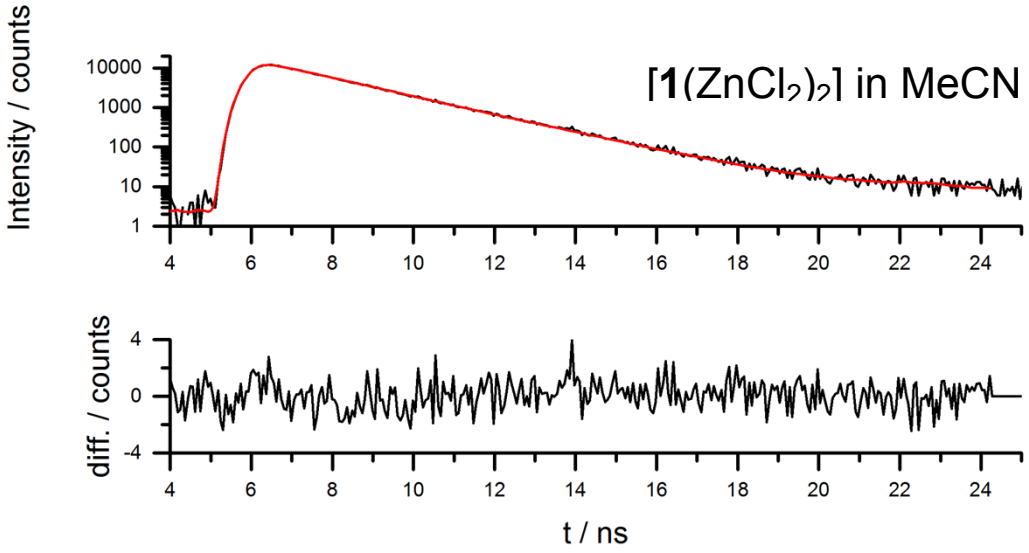

absorption
emission
30000
25000
20000
15000
10000
5000
0
ε / L mol⁻¹cm⁻¹
150
100
50
0
emission / a.u.
300
400
500
600
700
800
λ / nm

Figure S4. Lifetime decay curves for compounds **1** and **5** and the respective $ZnCl_2$ complexes [**1**$(ZnCl_2)_2$] and [**5**$(ZnCl_2)$] (IRF standard: LUDOX®). Fluorescence excitation was performed with a 280 nm pulsed LED at 10 MHz repetition rate.
Shown are the respective decay curves measured in acetonitrile, the model fit curve and the residuals (χ^2 was 1.00±0.05 for all fits). Amplitude weighted average lifetimes are τ_{Av} = 4.6(2) ns (**1**), τ_{Av} = 7.6(6) ns (**5**), τ_{Av} = 1.8(4) ns ([**1**$(ZnCl_2)_2$]), τ_{Av} = 1.3(5) ns ([**5**$(ZnCl_2)$]).
Interestingly, the average lifetimes are nearly independent of the excitation wavelength in acetonitrile. When using a 450 nm pulsed LED, amplitude weighted average lifetimes are τ_{Av} = 4.6(8) ns (**1**), τ_{Av} = 7.9(3) ns (**5**), τ_{Av} = 1.8(4) ns ([**1**$(ZnCl_2)_2$]), τ_{Av} = 1.3(4) ns ([**5**$(ZnCl_2)$]).



c


[1(ZnCl2)2] in MeCN
Intensity / counts
10000
1000
100
10
1
4
6
8
10
12
14
16
18
20
22
24
diff. / counts
4
0
-4
t / ns

d

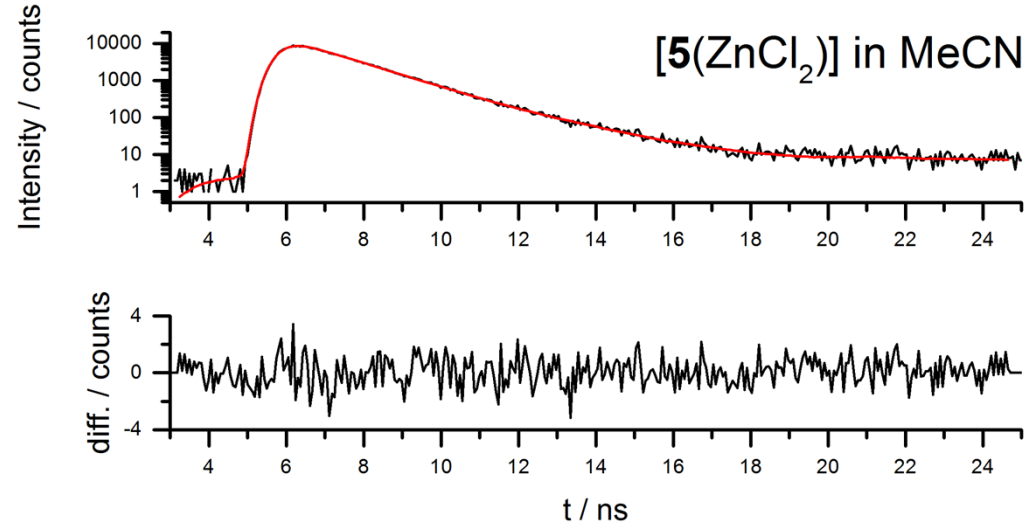

[5(ZnCl2)] in MeCN
Intensity / counts
10000
1000
100
10
1
4
6
8
10
12
14
16
18
20
22
24
diff. / counts
4
0
-4
t / ns

Figure S5. Comparison between the UV/Vis spectra of [**1**$(CuI)_2$] in CH_2Cl_2 and CH_3CN solutions.

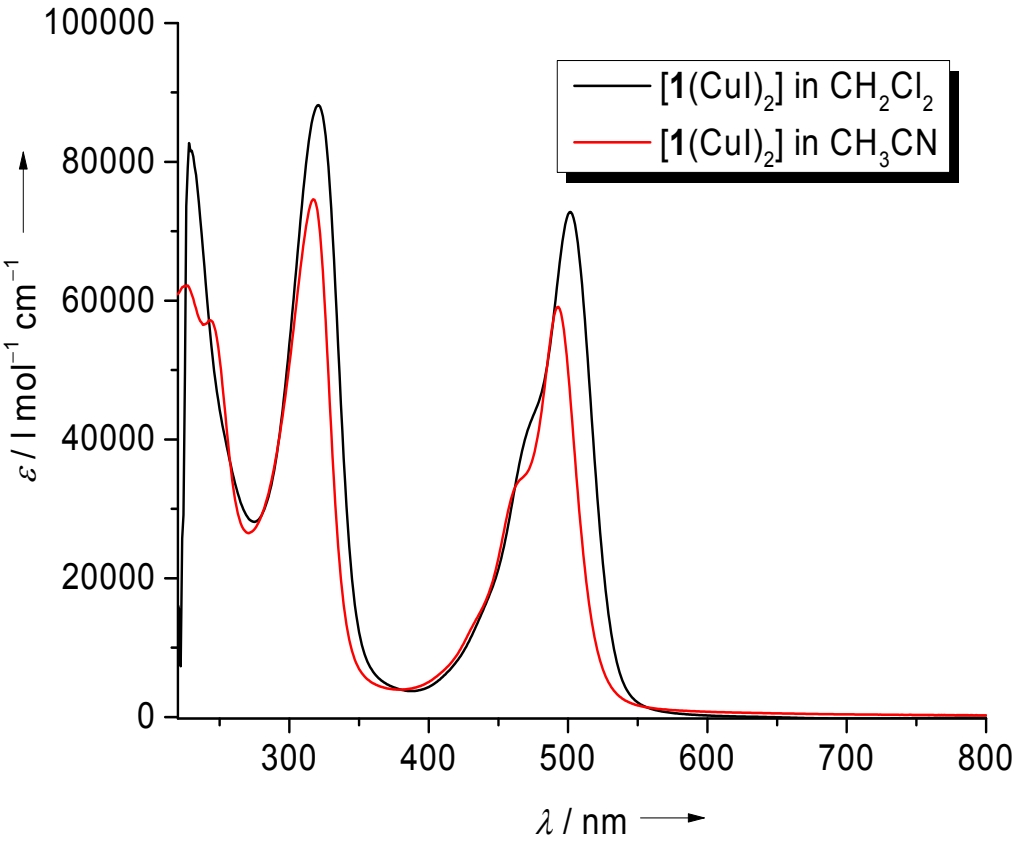


Figure S6. Absorption spectra for addition of a $ZnCl_2$ solution (1µL = 0.2 eq.) to a $0.64 \cdot 10^{-5}$ mol/l solution (3 mL) of [**1**$(ZnCl_2)_2$] in CH_2Cl_2.

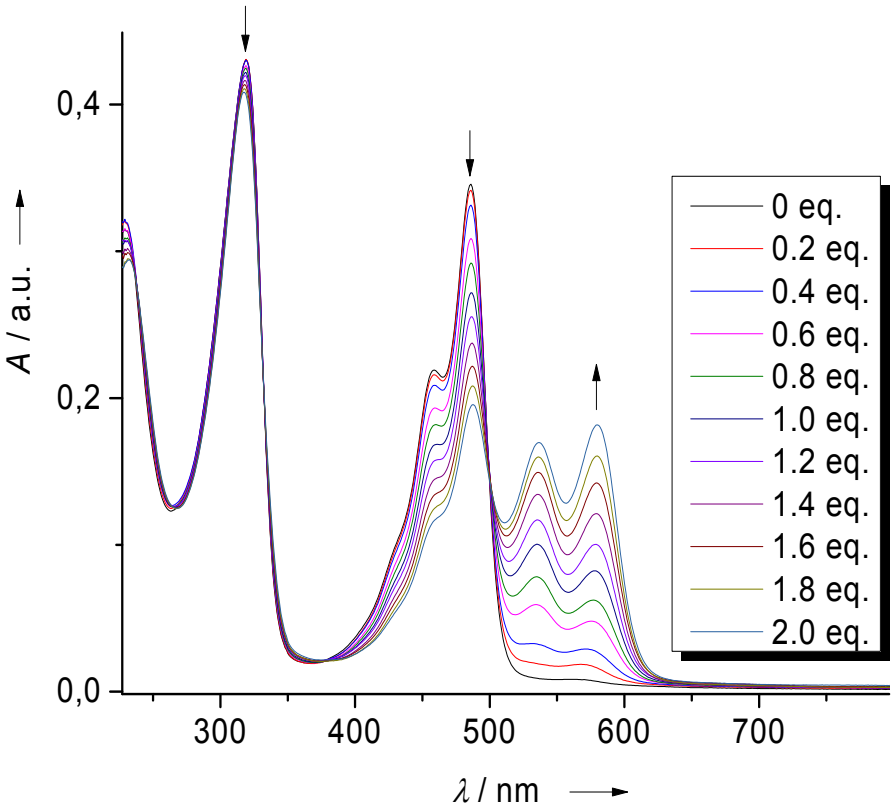


Figure S7. Diffuse reflectance spectrum of the solid coordination polymer ($[\mathbf{1}(ZnCl_2)_3]_n$) precipitating in the course of reaction of $[\mathbf{1}(ZnCl_2)_2]$ with an excess of $ZnCl_2$. The solid was embedded in a $BaSO_4$ matrix. For comparison, the spectrum of **1** in CH_3CN solution is shown underneath.

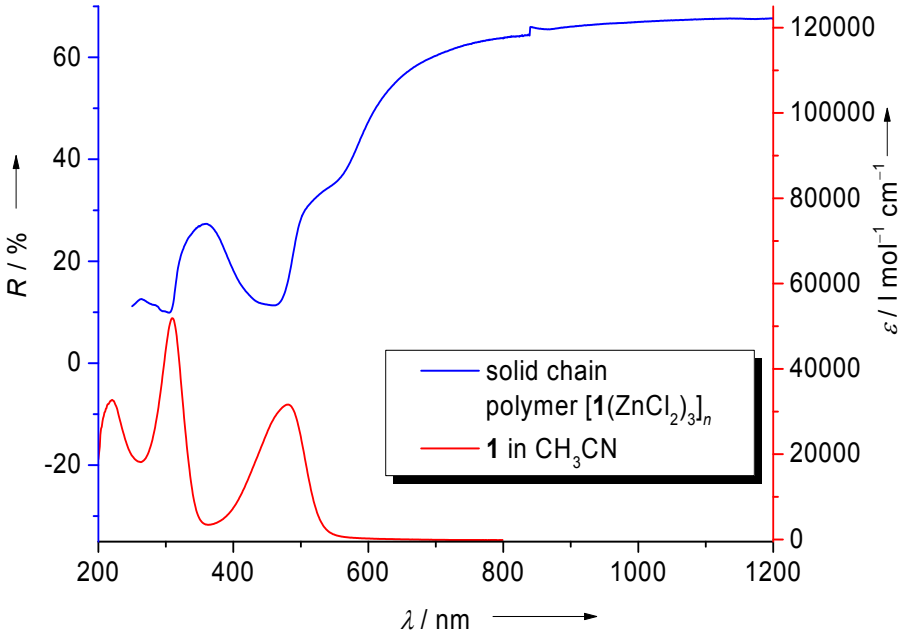


Table S1. Comparison between the experimentally determined and calculated bond distances (in Å) for the new compound **1**. See Figure **1** for the atom numbers. This calculations should test the quality of the calculations.

bond distances [Å]	exp.	Gaussian B3LYP/6-311G**	Turbomole BP/def2-SV(P)
N1-C1	1.395(4)	1.397	1.385
N1-C7	1.302(4)	1.292	1.303
N2-C7	1.390(4)	1.392	1.396
N3-C7	1.363(4)	1.390	1.403
N4-C2	1.403(4)	1.393	1.385
N4-C12	1.298(4)	1.289	1.303
N5-C12	1.382(4)	1.390	1.396
N6-C12	1.390(4)	1.396	1.403
N7-C4	1.346(4)	1.342	1.351
N7'-C5	1.354(4)	1.341	1.351
C1-C2	1.457(5)	1.458	1.471
C1-C6	1.382(4)	1.378	1.398
C2-C3	1.371(5)	1.377	1.398
C3-C4	1.426(4)	1.420	1.428
C4-C5	1.435(4)	1.443	1.459
C5-C6	1.417(4)	1.421	1.428

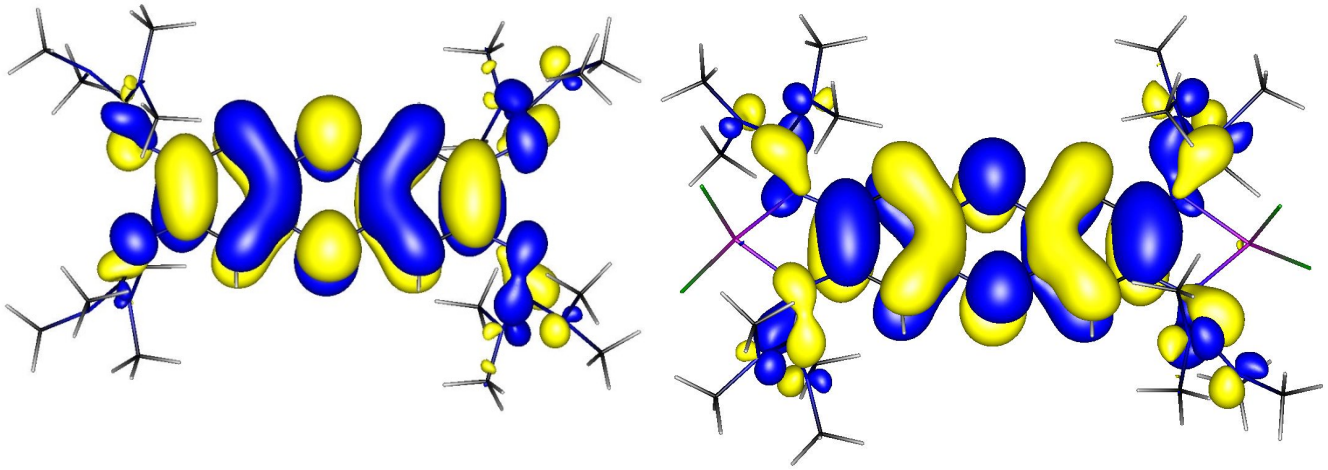
Table S2. Contributions of the valence orbitals to the electronic transitions in **1**, [**1**$(ZnCl_2)_2$] and [$(\mathbf{1})_2(ZnCl_2)_5$] as calculated with B3LYP/def2-SV(P).

	wavenumber of transition (nm)	orbital number, occcupied orbital	orbital number, acceptor orbital	contribution (%)
1	440.76	235(HOMO)	236(LUMO)	94.0
[**1**$(ZnCl_2)_2$]	461.57	171(HOMO)	172(LUMO)	92.6
[$(\mathbf{1})_2(ZnCl_2)_5$]	503.02	502 501 502 (HOMO) 501	504 503 503 (LUMO) 504	44.4 37.4 7.2 5.4
	500.78	501 501 502 502 499 500 499	503 504 504 503 504 503 503	19.7 19.2 18.4 13.1 11.9 5.7 4.5
	496.16	500 499 500 499 501 501 502	503 504 504 503 504 503 504	39.4 15.7 11.9 7.7 7.0 6.6 6.1

Figure S8. Visualization of the HOMO and LUMO of **1** and [**1**$(ZnCl_2)_2$] (B3LYP/def2-SV(P) calculations).

1 [**1**$(ZnCl_2)_2$]

LUMO



HOMO

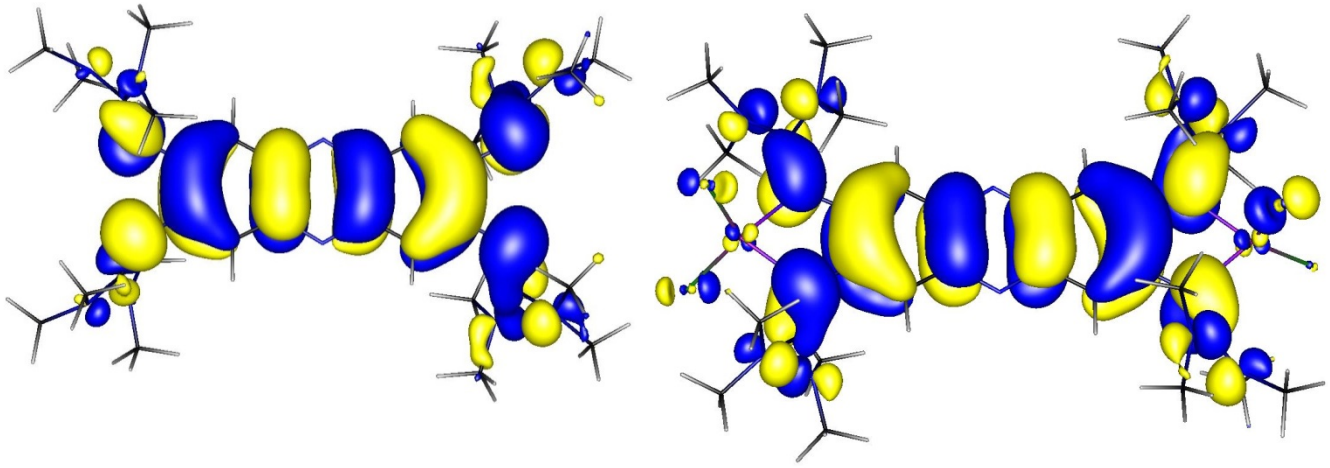
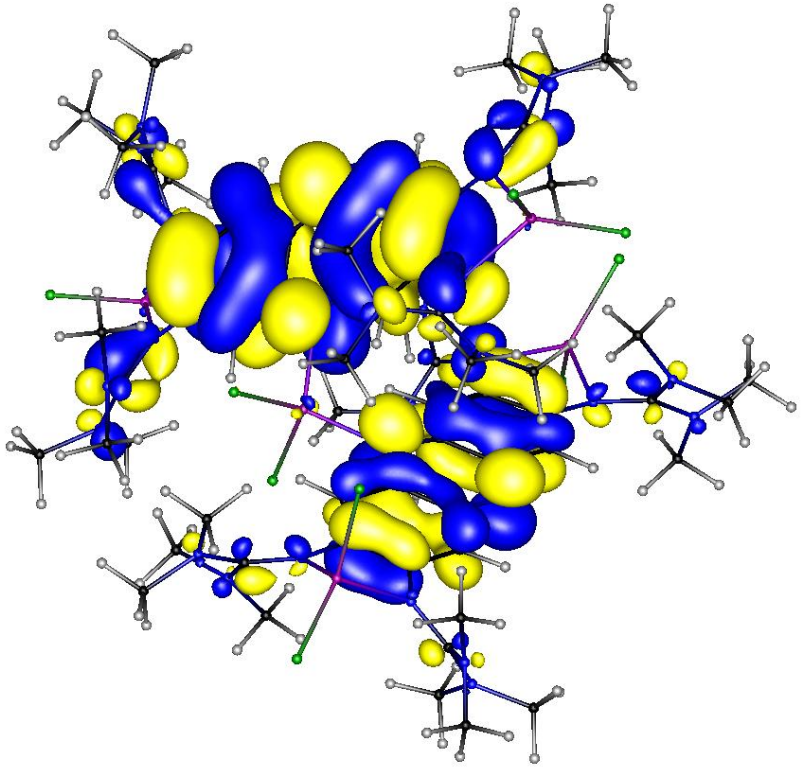


Figure S9. Visualization of the isodensity surfaces for the HOMO and LUMO of $[(\mathbf{1})_2(ZnCl_2)_5]$ (B3LYP/def2-SV(P) calculations).

LUMO



HOMO

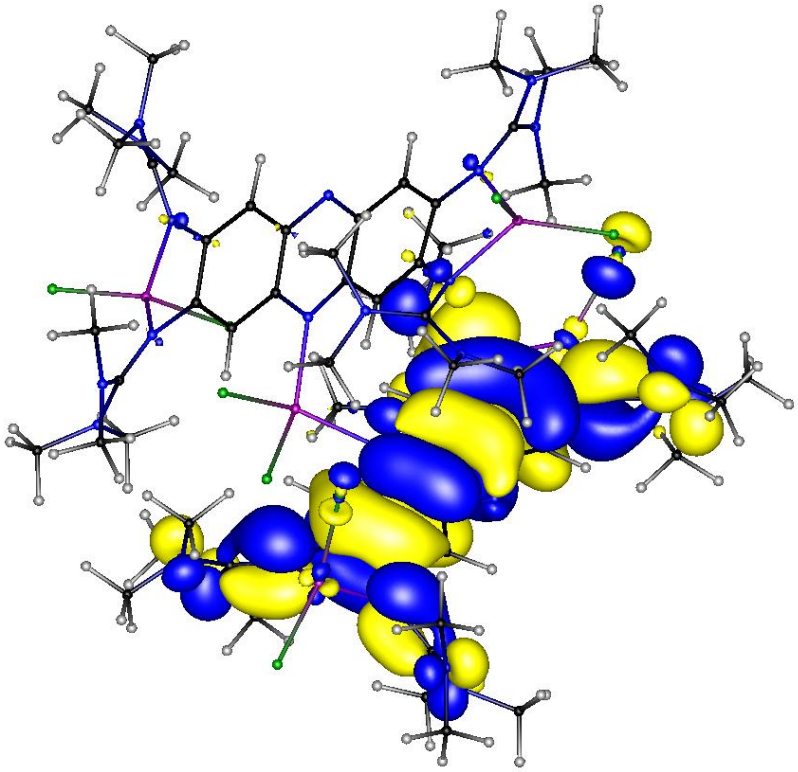
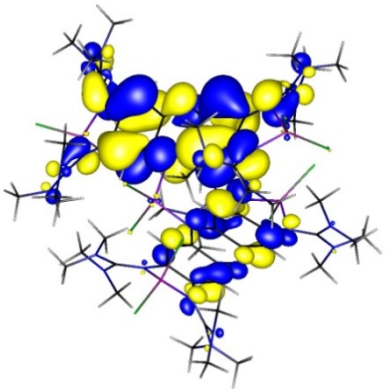
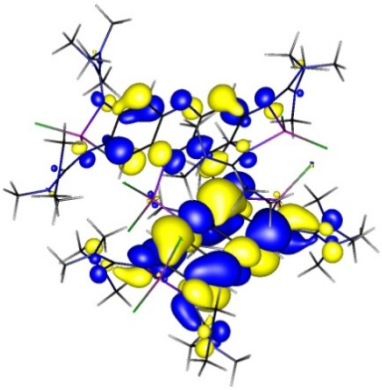


Figure S10. Visualization of the isodensity surfaces for the orbitals contributing to the electronic transitions (B3LYP/def2-SV(P), see also Table S1).



499



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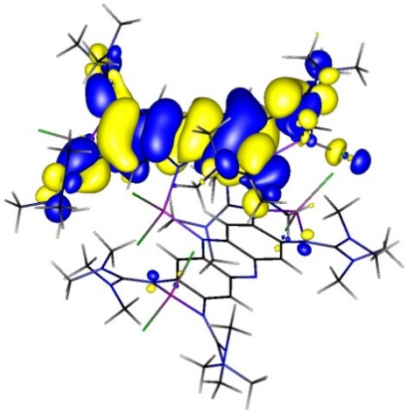

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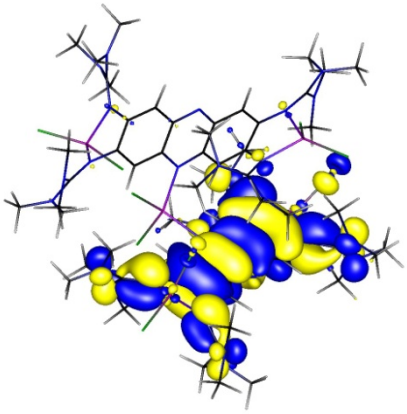
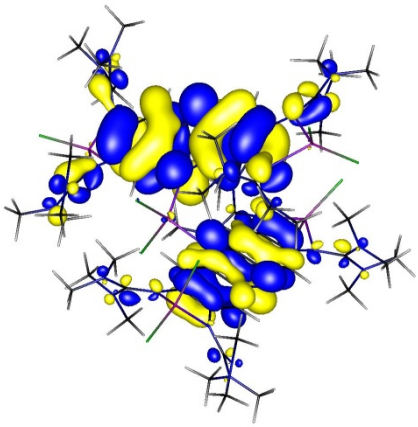
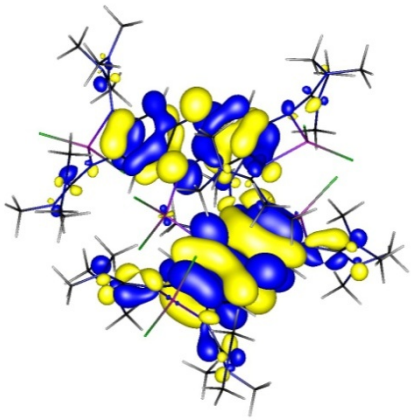


502 HOMO



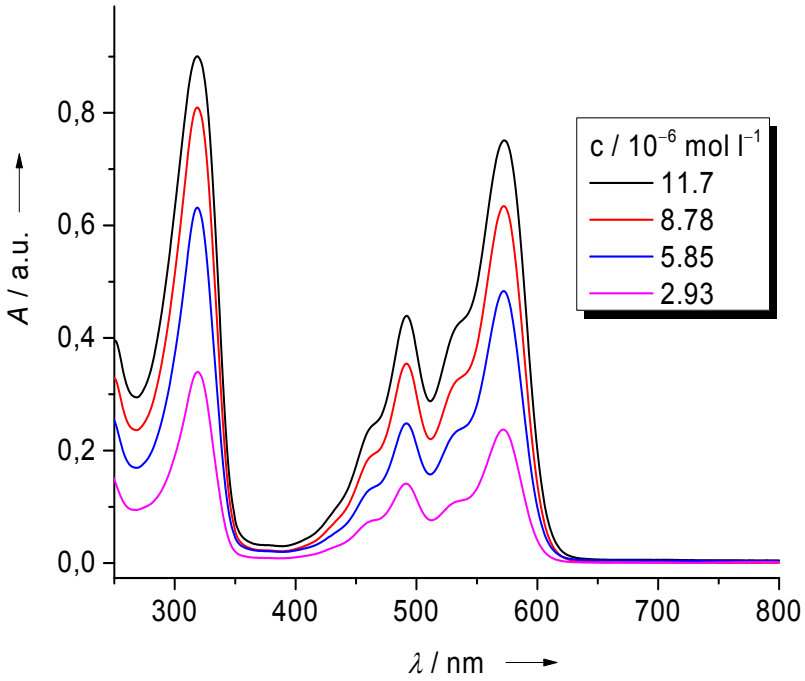
503 LUMO



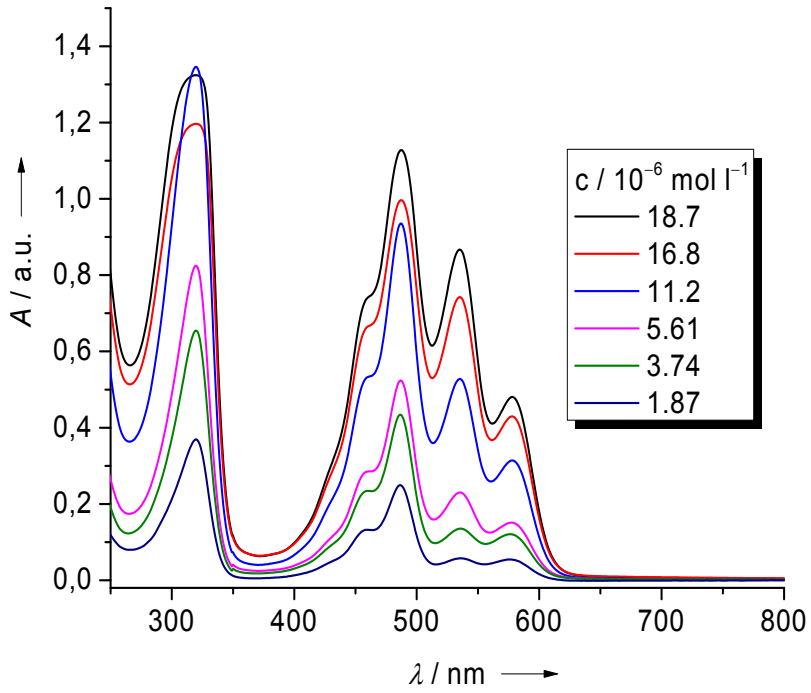
504

Figure S11. UV/Vis spectra recorded for experiments, in which the product from reaction between [**1**$(ZnCl_2)_2$] and 0.5 eq. of $ZnCl_2$ (the stoichiometry of [$(\mathbf{1})_2(ZnCl_2)_5$]) was dissolved in several concentrations in different solvents.

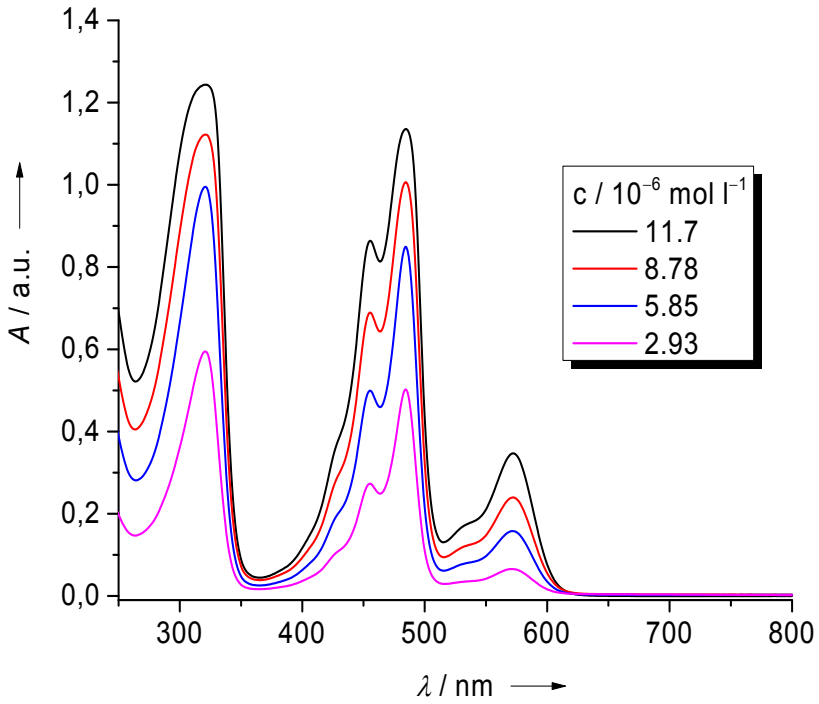
Solvent: $CHCl_3$



Solvent: CH_2Cl_2



Solvent: THF


1,4
1,2
1,0
0,8
0,6
0,4
0,2
0,0
A / a.u.
300
400
500
600
700
800
λ / nm
c / 10⁻⁶ mol l⁻¹
11.7
8.78
5.85
2.93