Supporting Information

Coordinative Self-Assembly into Fluorescent Ultrathin Films

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Synthesis of ligand 1 and polymer 6

2,6-Bis(1´-methylbenzimidazolyl)-4-hydroxypyridine 1: 3.94 g (19.51 mmol) Pyridine-2,6-dicarboxylic acid (chelidamic acid) and 5.27 g (19.51 mmol) N-methyl-1,2-phenylenediamine were added to 16 mL phosphoric acid (85 %) under nitrogen and stirred at 205 °C for 14 h. After cooling to room temperature the dark blue mixture was poured into 600 mL water and stirred until a light blue precipitate formed. The precipitate was filtered off and resuspended in 500 mL of hot 10% aqueous sodium carbonate solution. The suspension was stirred until it turned pink. Then the pink solid was filtered off, washed twice with water and dissolved in 300 mL hot methanol. The dark pink methanol solution was neutralized with 1 M HCl until it turned dark blue. After standing in a refrigerator over night grey feathery crystals of the product appeared, which were filtered from the dark blue solution and dried. Yield: 4.40 g (64 %), m. p. 282 °C.

^{1}H NMR (d_6-DMSO, 300 MHz): δ (ppm) 4.25 (s, 6H); 7.5 (m, phenyl-H, 4H); 7.8 (dd, phenyl-H, 4H); 7.9 (s, phenyl-H, 2H), 12.2 (s, OH).

Polymer 6: 0.100 mg (0.168 mmol) of **4**, 0.098 mg (0.168 mol) 1,4-dibromo-2,5-bis(6-bromohexyloxy)benzene **2**, 3 mol % $Pd(PPh_3)_4$ in 2 mL toluene were added to and purged with nitrogen for 15 minutes. To the mixture were added 0.14 g (2.02 mmol) K_2CO_3 und 12 mg Alliquat® 336 in 1 mL water and heated to 100 °C 6 h. After this were added of 1 mL toluene and 1 mL H_2O to the mixture and heated 18 h. After cooling to room temperature the reaction mixture was diluted with 30 mL toluene and extracted with brine. The organic phase was dried over $MgSO_4$ and filtered over celite to remove residual palladium. After concentration in vacuum the residue was poured into 150 mL methanol to precipitate the polymer. The polymer was filtered and dried in vacuum. Yield: 100 mg (98 %), m. p. 85 °C.

^{1}H NMR (d_1-$CHCl_3$, 300 MHz): δ (ppm) 0.78 (s, 12H), 1,14 (s, 6H), 1.43 (m, 8H), 1.57 (s, 6H), 1.74 (s, 4H), 1.83 (dd, 4H), 2.04 (s, 4H), 3.40 (m, 4H), 3.99 (m, 4H), 4.14 (s, 2H), 7.58 (m, phenyl-H, 2H), 7.7 (m, phenyl-H, 2H), 7.8 (m, phenyl-H, 2H).

^{13}C NMR (d_1-$CHCl_3$, 300 MHz): δ (ppm) 1.08, 14.12, 14.15, 22.71, 22.77, 22.79, 23.84, 24.07, 25.00, 25.26, 25.34, 27.79, 27.85, 27.94, 29.08, 29.19, 29.31, 29.85, 29.99, 30.04, 31.63, 31.77, 32.75, 32.78, 33.74, 33.95, 40.37, 40.61, 55.09, 69.58, 69.69, 70.05, 77.32, 83.67, 110.19, 111.11, 116.57, 116.86, 118.67, 119.05, 119.35, 119.75, 124.17, 124.40, 127.96, 128.06, 128.49, 128.52, 128.88, 131.42, 132.05, 132.12, 133.81, 135.07, 137.00, 139.86, 150.45.

Anal. Calcd. for $C_{45}H_{64}Br_2O_2$: C, 67.18; H, 7.87. Found: C, 66.72; H, 7.56.

GPC: M_n = 3700, M_w = 7500, polydispersity: 2.04.

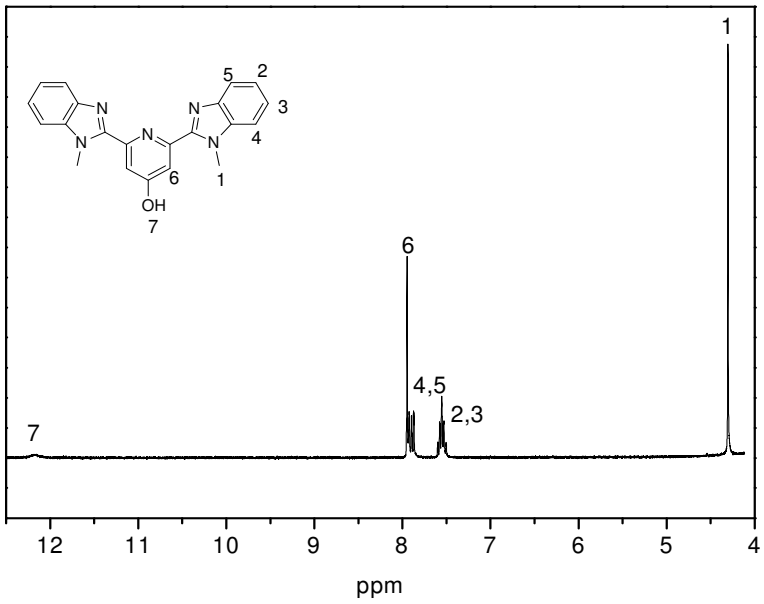


Fig. S1: ^{1}H NMR spectrum of **1** in d_6-DMSO .

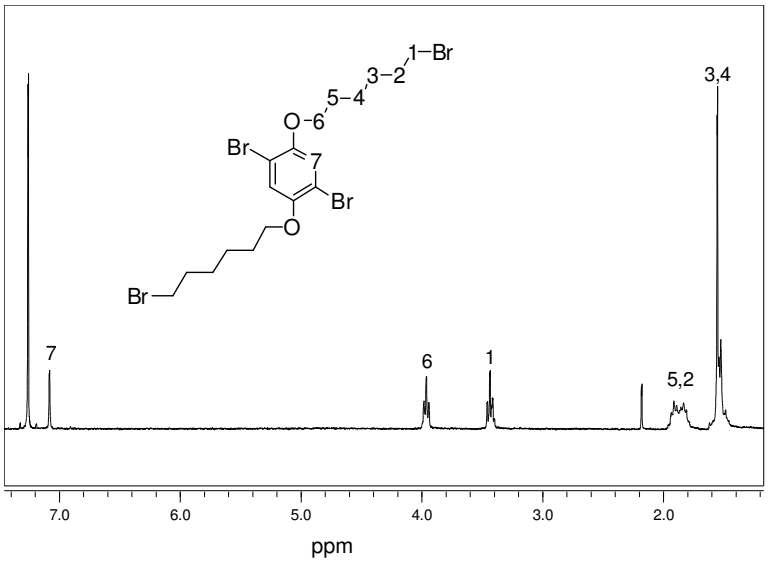


Fig. S2: ^{1}H NMR spectrum of **2** in deuterated chloroform.

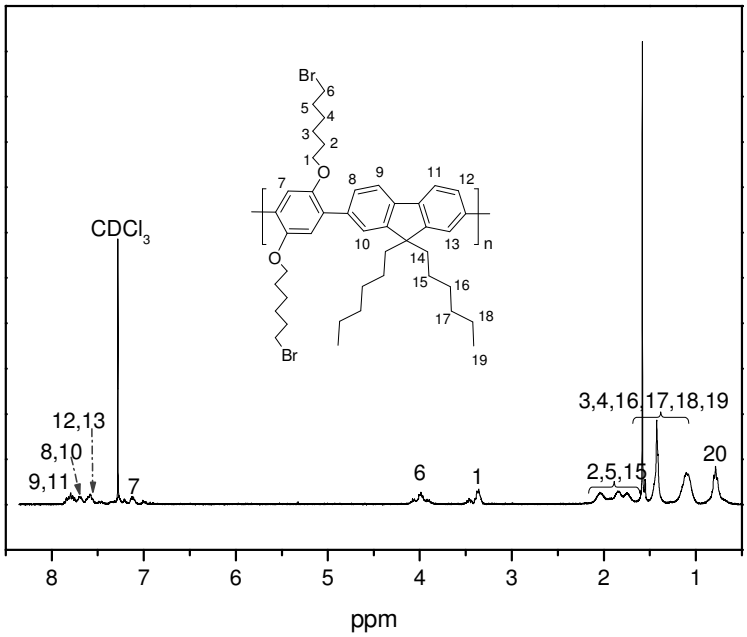


Fig. S3: ^{1}H NMR spectrum of **6** in deuterated chloroform.

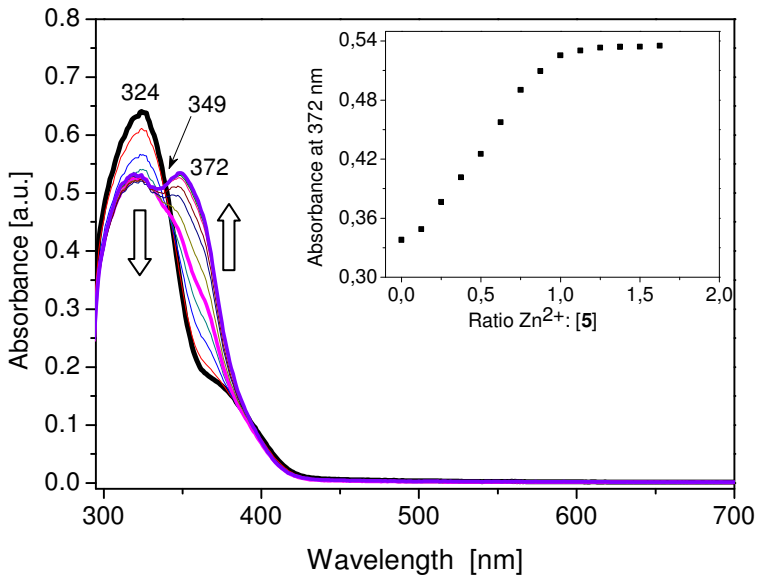
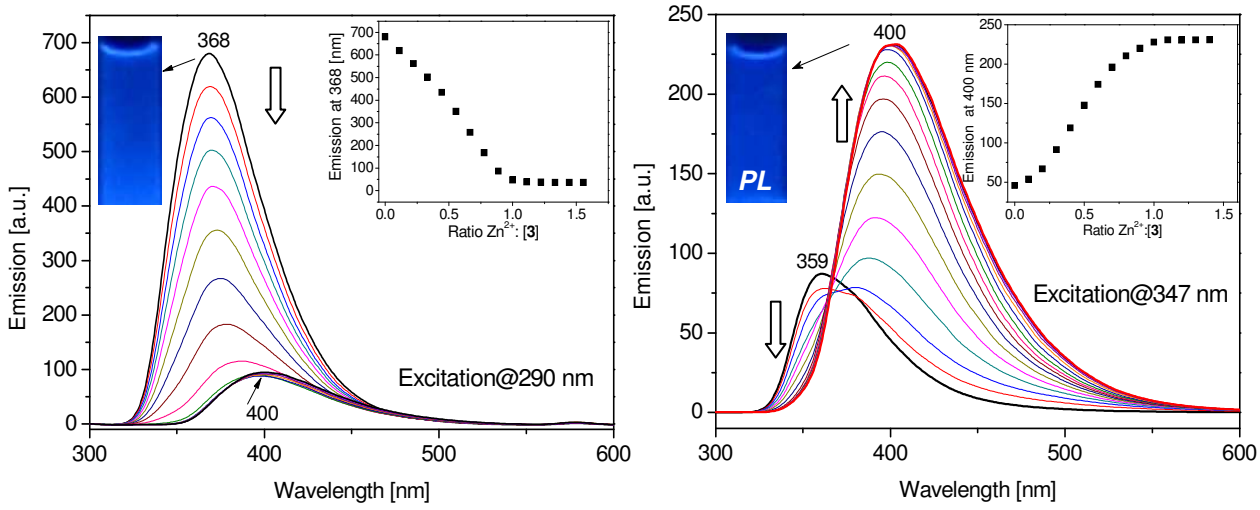


Fig. S4: UV/vis absorption spectra of polymer **5** (conc.: 1.09 x 10^{-4} mol L^{-1}) in acetonitrile/chloroform (9:1 v/v) before and after addition of 1 µL-aliquots of zinc perchlorate (conc.: 1.24 x 10^{-3} mol L^{-1}) in acetonitrile/chloroform (9:1 v/v).



(a) **(b)**

Figure S5: Change of fluorescence of monomer **3** (conc.: 4.46 x 10^{-4} mol L^{-1}) in acetonitrile/chloroform (9:1 v/v) before and after addition of 1 µL-aliquots of zinc perchlorate (conc.: 1.24 x 10^{-3} mol L^{-1}) in acetonitrile/chloroform (9:1 v/v). The inset shows the absorbance at 368 nm versus the zinc: ligand molar ratio in solution.

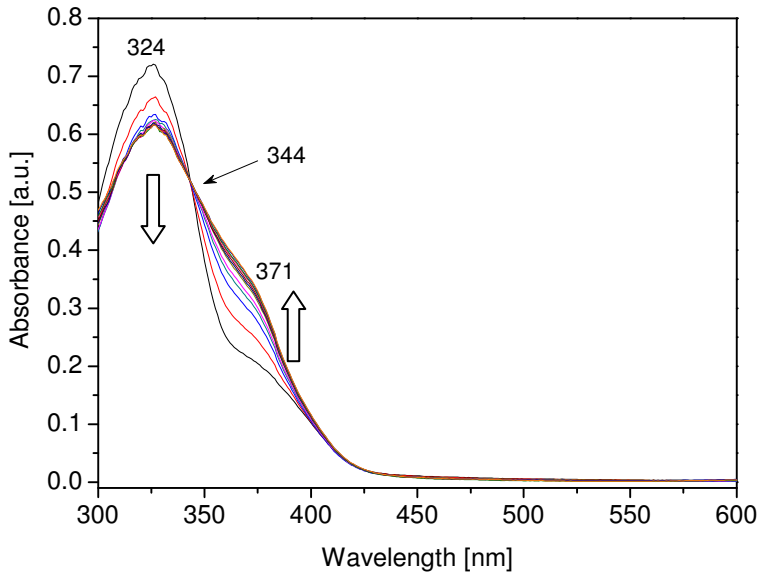


Fig. S6: UV/vis absorption spectra of polymer **5** (conc.: 1.09 x 10^{-4} mol L^{-1}) in $CHCl_3/CH_3CN$ (1:9 v/v) before and after addition of 1 µL-aliquots of copper acetate (conc.: 2.48 x 10^{-3} mol L^{-1}) in $CHCl_3/CH_3CN$ (1:9 v/v).

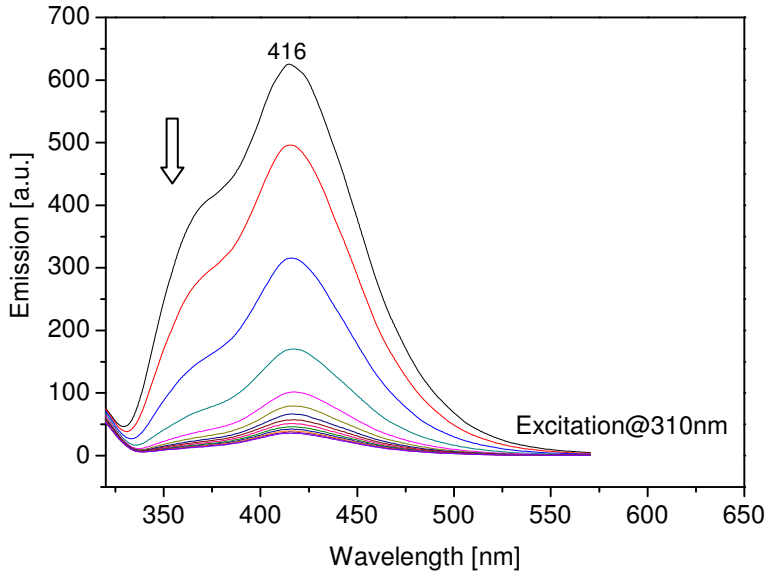
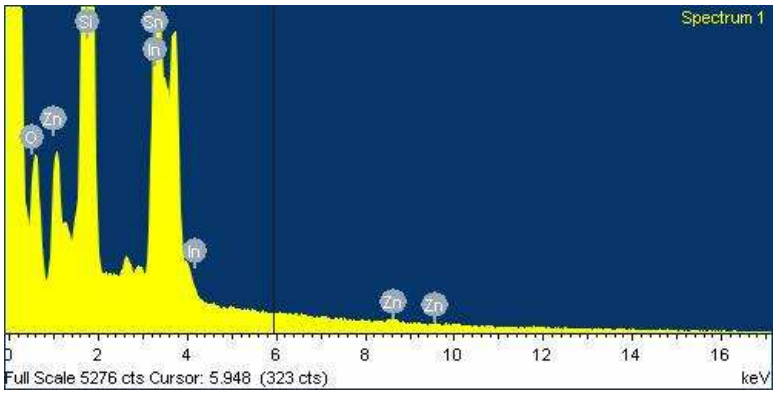


Fig. S7: Change of fluorescence of polymer **5** (conc.: 1.09 x 10^{-4} mol L^{-1}) in $CHCl_3/CH_3CN$ (1:9 v/v) before and after addition of 1 µL-aliquots of copper acetate (conc.: 2.48 x 10^{-3} mol L^{-1}) $CHCl_3/CH_3CN$ (1:9 v/v).



Element	Weight%	Atomic%
O	17.243	5.70
Si	45.095	3.18
Zn	**1.14**	**0.58**
In	36.021	0.39
Sn	0.50	0.14

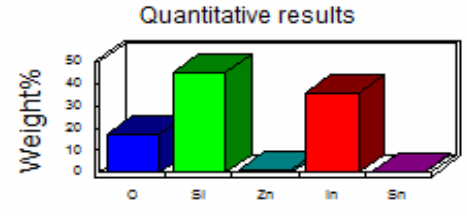
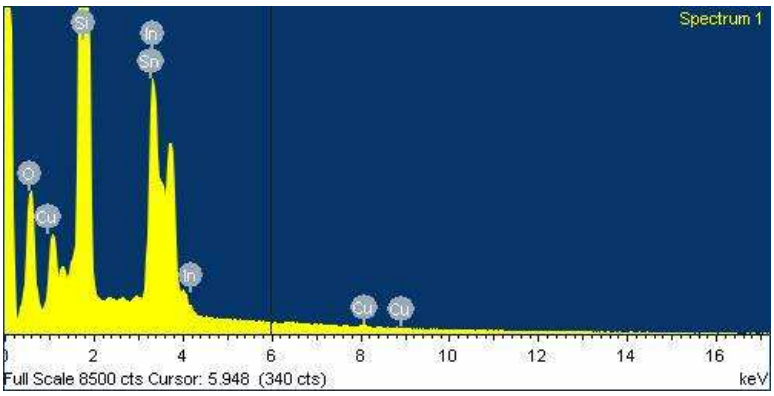


Fig. S8: EDX spectrum and elemental composition of layer-by-layer assembled film of polymer **5**/zinc complex: 1.1, 8.6 und 9.6 keV.



Element	Weight%	Atomic%
O	32.315	5.99
Si	36.963	6.49
Cu	**0.59**	**0.26**
In	28.50	6.88
Sn	1.64	0.38

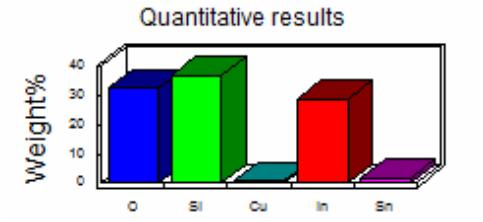


Fig. S9: EDX spectrum and elemental composition of layer-by-layer assembled film of polymer **5**/copper complex: Cu: 1.0, 8.1 und 8.9 keV.