

## Supporting Information

# Turning weak emitters into outstanding luminescent materials using rigid host media

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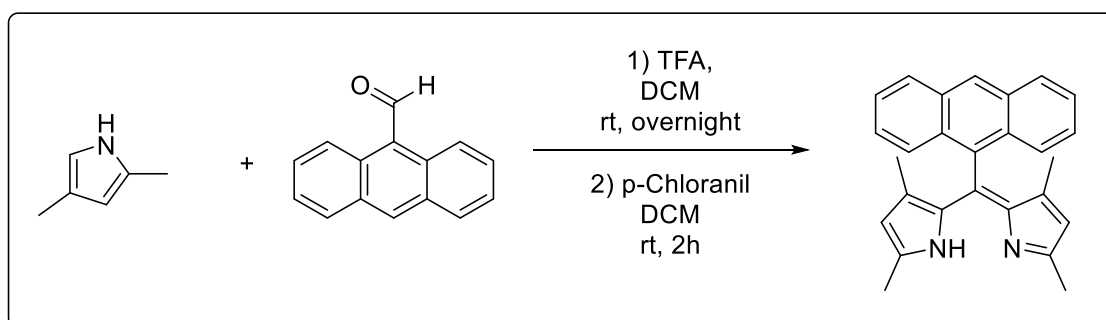
#### Supporting Figures

## Experimental Section

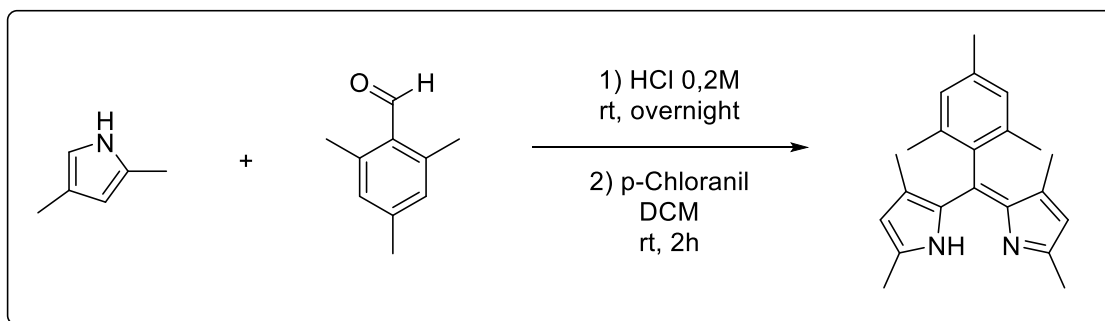
### Materials and Methods

All air- and water-sensitive experiments were performed under a nitrogen atmosphere by using standard vacuum-line techniques. All chemicals were obtained commercially (Sigma Aldrich, Acros organics and Honeywell) and used without further purification. "H<sub>2</sub>O" refers to high purity water with conductivity of 0.04  $\mu\text{S cm}^{-1}$ , obtained from a Milli-Q purification system. Thin-layer chromatography (TLC) was carried out on silica plates (silica gel 60 F254, Merck 5554) and visualized by UV lamp (254 nm). Preparative column chromatography was carried out using silica gel (Merck Silica Gel 60, 230:400 mesh) pre-soaked in the starting eluent. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with either Bruker Ascend 300 or Bruker 500 Ascend spectrometers operating at 25 °C. CDCl<sub>3</sub> was used as internal standard for both <sup>1</sup>H NMR ( $\delta_{\text{H}} = 7.26$  ppm) and <sup>13</sup>C NMR ( $\delta_{\text{C}} = 77.16$  ppm) spectra. Fluorescence spectra and lifetimes were measured using an Edinburgh FLS980 photoluminescence spectrometer, equipped with a 450 W Xenon arc lamp, Czerny Turner excitation and emission monochromators (1.8 nm/mm@1 dispersion; 1800 grooves/mm@1), time-correlated single photon counting (TCSPC) module and a Hamamatsu R928P photomultiplier tube (in fan assisted TE cooled housing, operating temperature -20 °C). For lifetime measurements, samples were excited with an EPL-475 (471.8 nm; 62.6 ps pulse width) picosecond pulsed diode laser and data analysis was performed on the F980 software with numerical data deconvolution based on Marquardt-Levenberg algorithm. Luminescence quantum yields were measured using as reference a basic ethanol solution of fluorescein. Transmission electron microscopy images were taken on a 100 kV CM100 TEM (FEI).

### Dipyrrromethene ligands synthesis

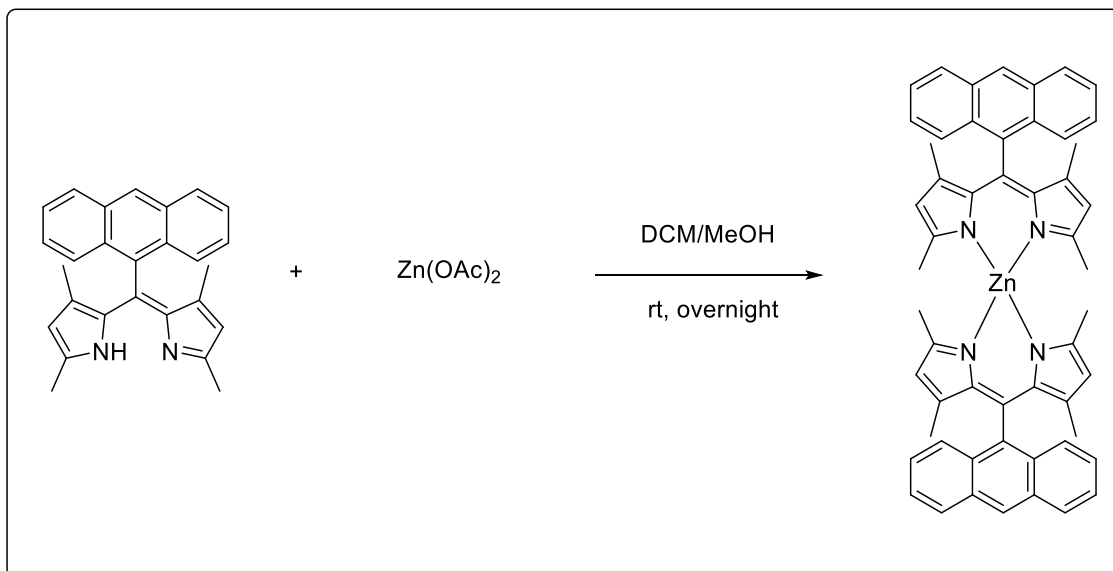


**L1.** To 20 mL of dry DCM, 2,4-dimethylpyrrole (1 mL, 9.71 mmol, 2,3 equiv.) was added, followed by the addition of the 9-anthracenecarboxaldehyde (866 mg, 4.20 mmol, 1 equiv.). 2 drops of trifluoromethylacetic acid (TFA) were added and the reaction mixture was stirred at room temperature and in dark. The reaction was monitored by thin-layer-chromatography (TLC). After the indicated time p-Chloranil (1032 mg, 4.20 mmol, 1 equiv.) was added. The reaction mixture was stirred at room temperature for 2 more hours. Distilled water (20 mL) was added and the mixture was extracted with DCM 3 times (10 mL). The organic phases were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and purified through alumina gel (Cyclohexane/Ethylacetate 95:5). A large orange fraction was collected, concentrated and recrystallized from DCM/MeOH. A brownish crystalline solid was obtained as the product (632 mg; 40% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  8.52 (s, 1H), 8.02-7.98 (m, 4H), 7.49-7.34 (m, 4H), 5.77 (s, 2H), 2.41 (s, 6H), 0.51 (s, 2H).

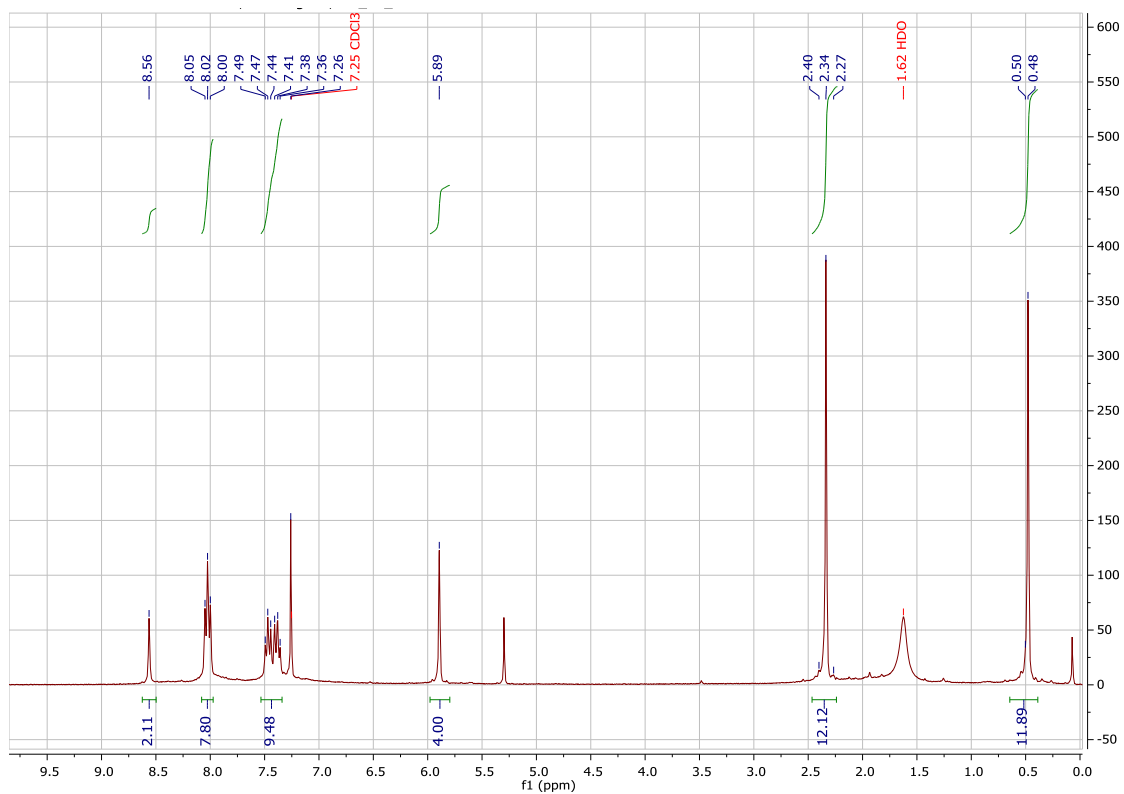


**L2.** To 25 mL of 0.2 M aqueous HCl, 2,4-dimethylpyrrole (1 mL, 9.71 mmol, 2,1 equiv.) was added, followed by the 2,4,6-trimethylbenzaldehyde (0.67 mL, 4.56 mmol, 1 equiv.). The reaction mixture was stirred at room temperature in dark. After 12 hours, a sticky solid was formed. 10 mL of dichloromethane (DCM) were added. The organic phase was separated and the water phase was extracted 3 times (10 mL) with DCM. The organic layers were combined, dried over anhydrous  $\text{Na}_2\text{SO}_4$  and filtered. The amount of solvent was reduced to 20 mL and p-Chloranil (1121 mg, 4.56 mmol, 1 equiv.) was added. The reaction mixture was stirred at room temperature for 2 more hours. 20 mL of water were added and the mixture was extracted with DCM 3 times (10 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$  and processed through alumina gel (Cyclohexane/Ethylacetate 95:5). A large orange fraction was collected, concentrated and recrystallized from DCM/ $\text{CH}_3\text{OH}$ , obtaining an orange crystalline solid (525 mg; 36% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  6.90 (s, 2H), 5.85 (s, 2H), 2.34 (s, 6H), 2.32 (s, 3H), 2.09 (s, 6H), 1.29 (s, 6H).

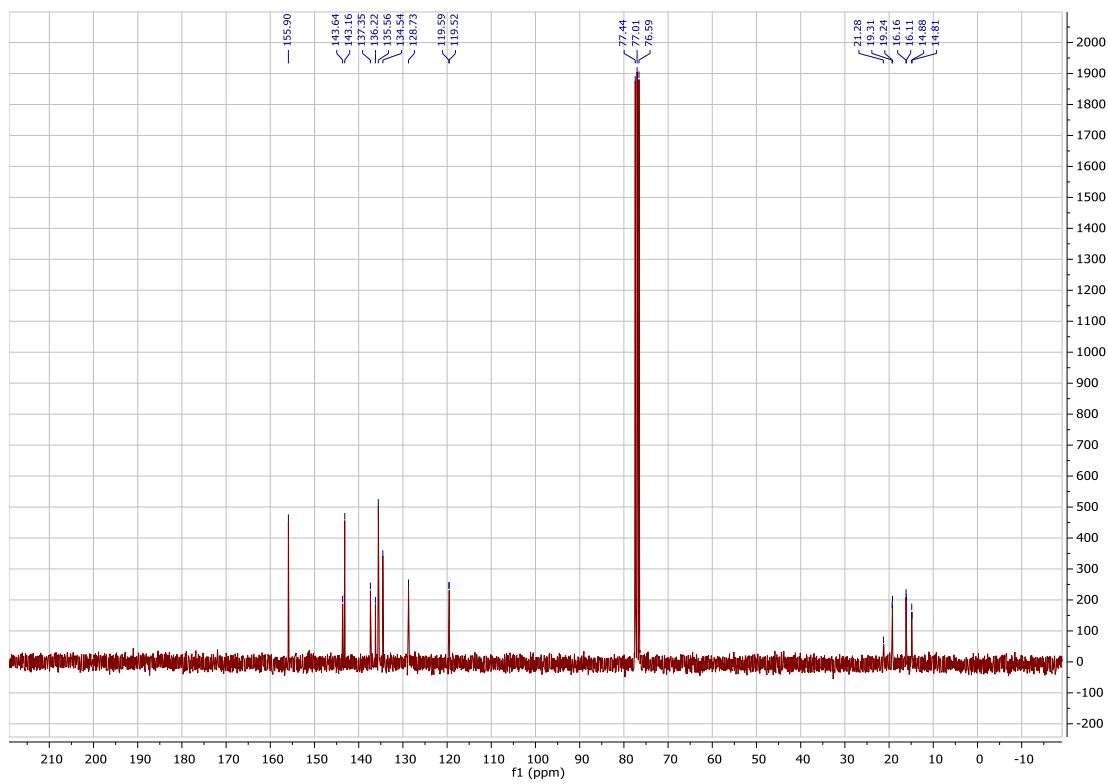
### Complexes synthesis



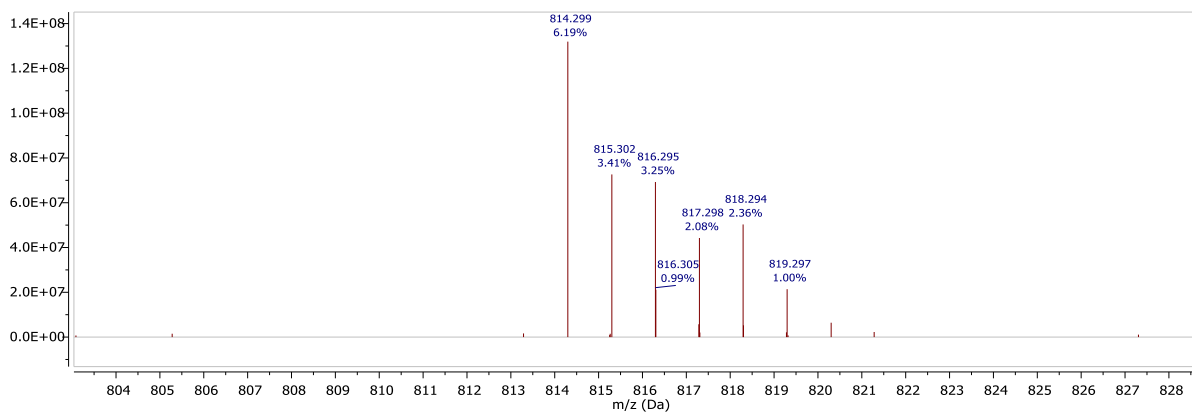
**1.** Following the general procedure, the reaction of **L1** (150 mg, 0.40 mmol, 2 equiv.) with zinc acetate (36 mg, 0.20 mmol, 1 equiv.) in a 2:1 mixture of DCM and Methanol gave **1** as an orange powder (146 mg; yield 89%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  8.57 (s, 2H), 8.02 (t,  $J = 7.4$  Hz, 8H), 7.43 (dt,  $J = 26.0, 6.8$  Hz, 8H), 5.89 (s, 4H), 2.34 (s, 12H), 0.48 (s, 12H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  156.79, 143.88, 140.78, 136.50, 131.60, 130.87, 126.32, 125.39, 120.35, 120.27, 16.55, 14.95. HR-ESI-MS: calcd for  $\text{C}_{54}\text{H}_{46}\text{N}_4\text{Zn}$  ( $\text{M}^+$ ): 814.301, found: 814.299.



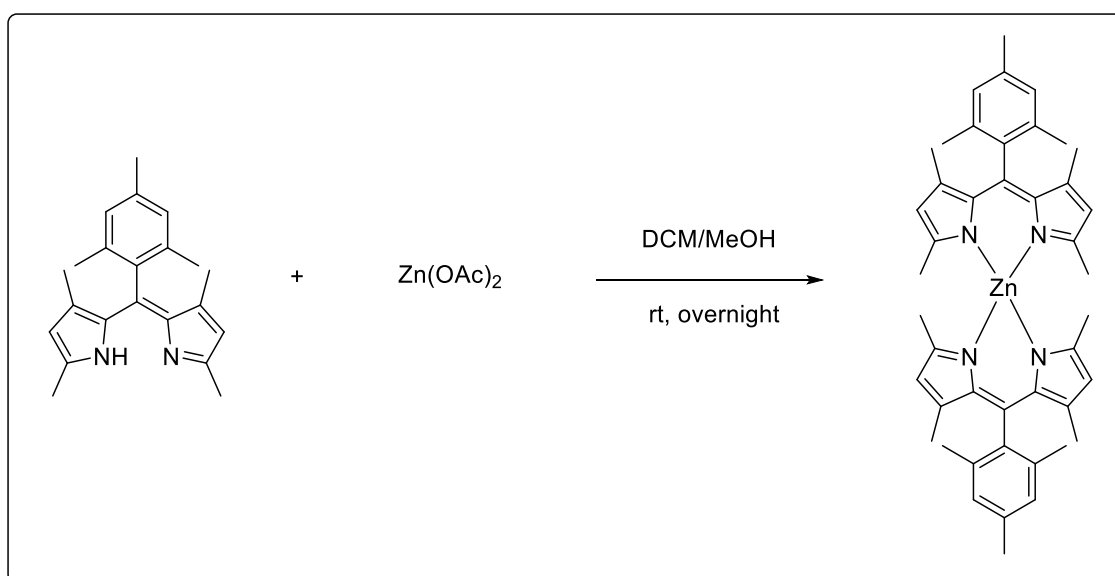
**Figure S1.**  $^1\text{H}$  NMR Spectrum of **1** in  $\text{CDCl}_3$ .



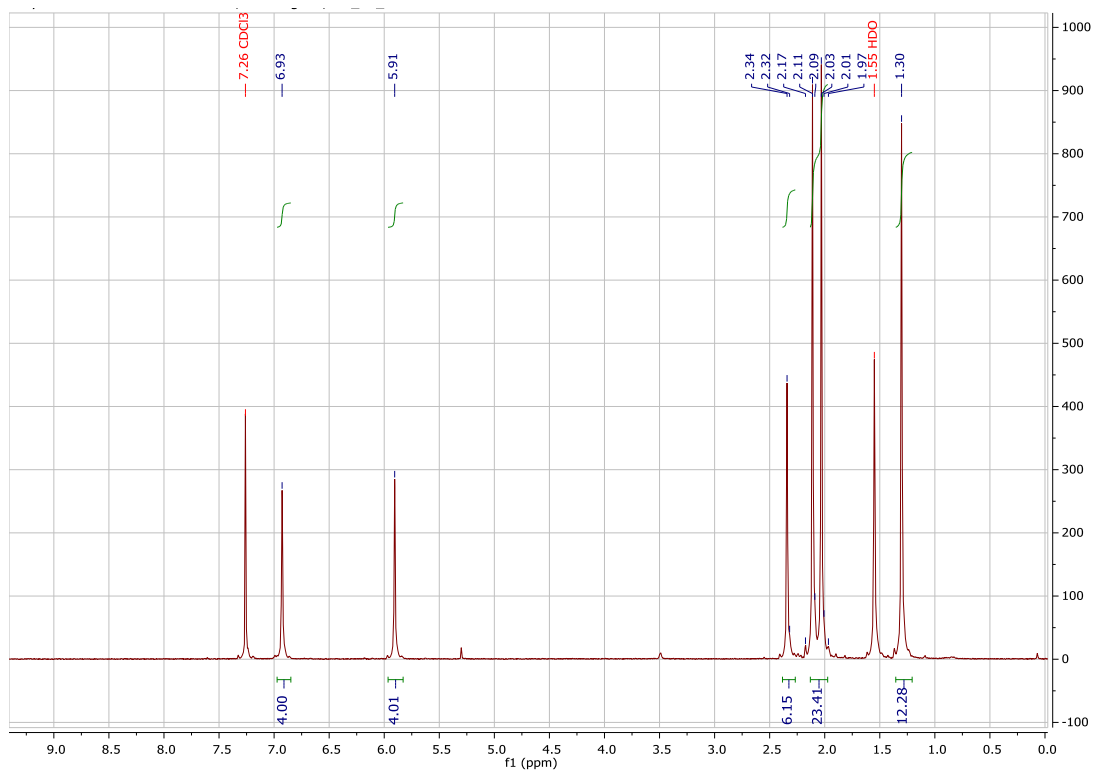
**Figure S2.**  $^{13}\text{C}$  NMR Spectrum of **1** in  $\text{CDCl}_3$ .



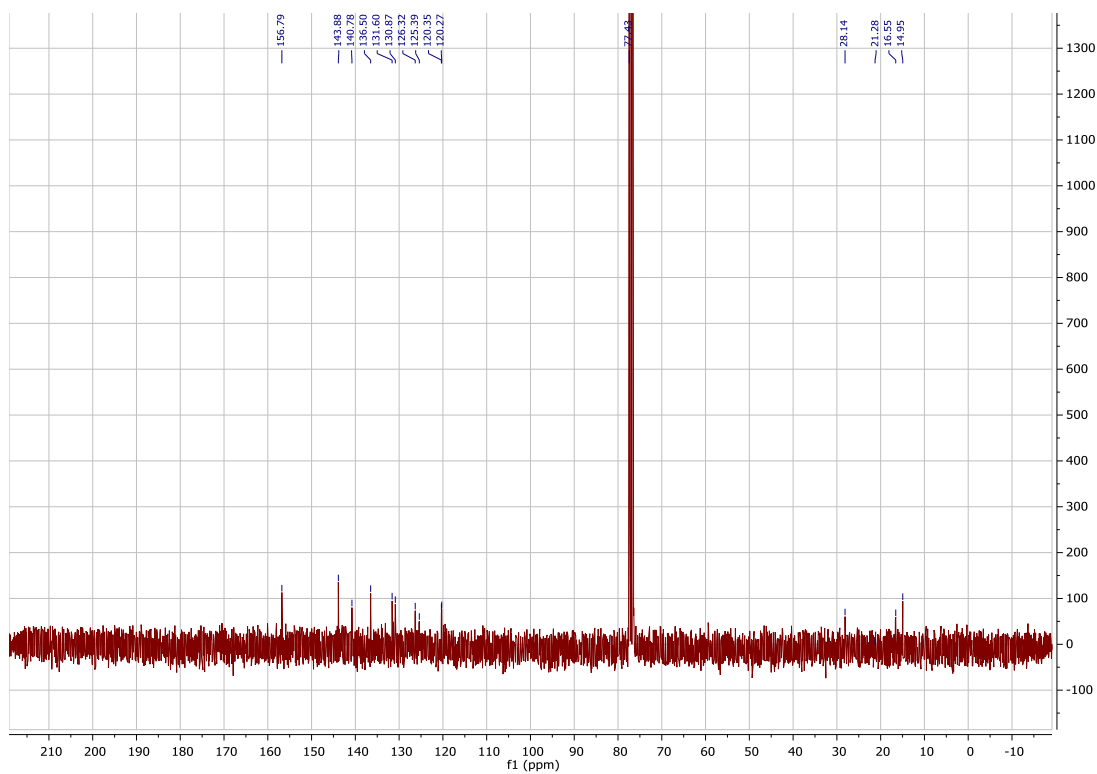
**Figure S3.** HR-ESI mass of **1** calcd for  $C_{54}H_{46}N_4Zn$  ( $M^+$ ): 814.301, found: 814.299.



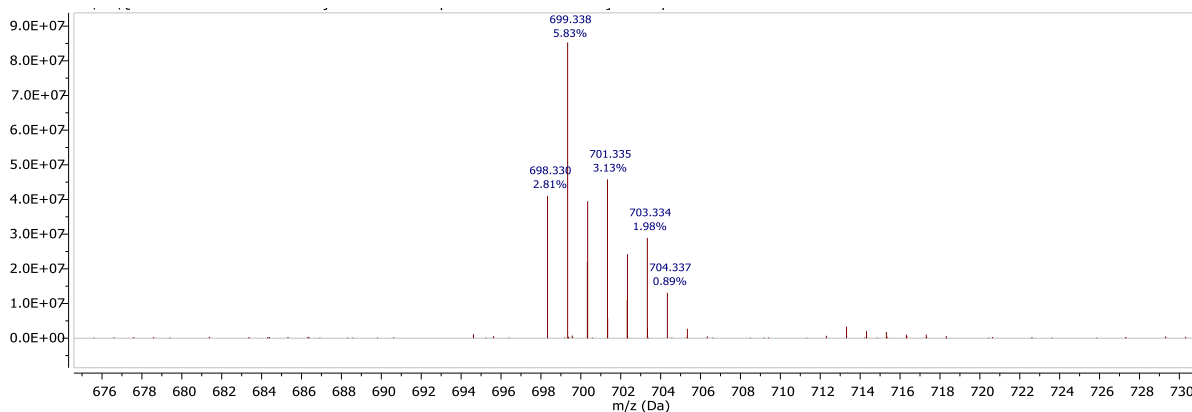
**2.** To a DCM solution (10 mL) of **L2** (105 mg, 0.32 mmol, 2 equiv.), was added a methanol (5 mL) solution of zinc acetate (30 mg, 0.16 mmol, 1 equiv.). After stirring overnight the solvent was reduced by a rotary evaporator. The orange precipitate was filtered and rinsed with cold methanol (105 mg; 91% yield).  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$  6.93 (s, 4H), 5.91 (s, 4H), 2.34 (s, 6H), 2.11 (s, 12H), 2.03 (s, 12H), 1.30 (s, 12H).  $^{13}C$  NMR ( $CDCl_3$ , 75 MHz)  $\delta$  155.90, 143.64, 143.16, 137.35, 136.22, 135.56, 134.54, 128.73, 119.59, 119.52, 21.28, 19.31, 19.24, 16.16, 16.11, 14.88, 14.81.



**Figure S4.**  $^1\text{H}$  NMR Spectrum of **2** in  $\text{CDCl}_3$ .



**Figure S5.**  $^{13}\text{C}$  NMR Spectrum of **2** in  $\text{CDCl}_3$ .



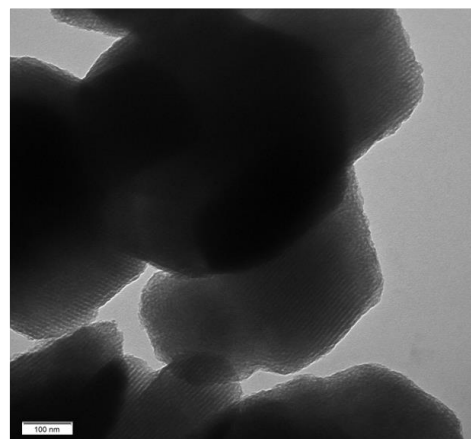
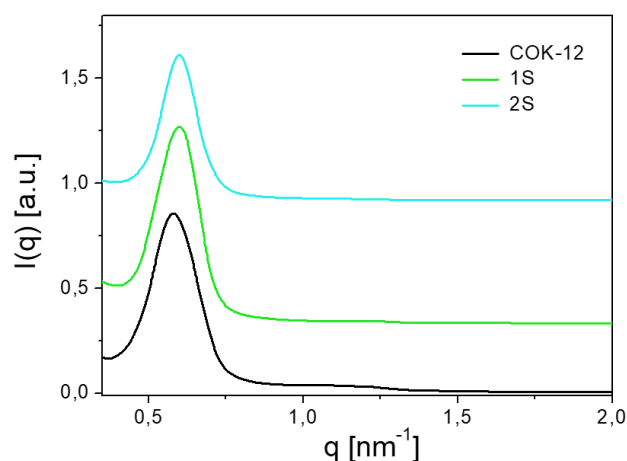
**Figure S6.** HR-ESI mass of **2** calcd for  $C_{44}H_{51}N_4Zn$  ( $MH^+$ ): 699.340, found: 699.338.

### Synthesis of dye-doped COK-12 silica samples 1S and 2S

Citric acid monohydrate (954 mg, 4.97 mmol) and trisodium citrate dihydrate (793.5 mg, 3.07 mmol), were dissolved in 27 ml of  $H_2O$ . To this solution, Pluronic-P123 and the dye **1** or **2** were added in a 99:1 ratio (0.169 mmol P123, 1.71 mmol **1** or **2**) and the resulting suspension was left stirring at room temperature overnight, during which time it turned into a clear solution with a slight orange tint. A sodium silicate water solution (1.8 mL, 21.97 mmol) was diluted with  $H_2O$  (7.5 mL) and added dropwise to the reaction mixture. The mixture was then stirred for 10 min, turning cloudy, and left undisturbed for 24 h, during which a white precipitate formed. Finally, the mixture was filtered under vacuum, the solid residue washed with  $H_2O$  repeatedly, until the foaming from the physisorbed surfactant ceased, and then dried in a vacuum desiccator overnight, leading to a light pink powdery solid, which photoluminesced bright green under UV-visible light.

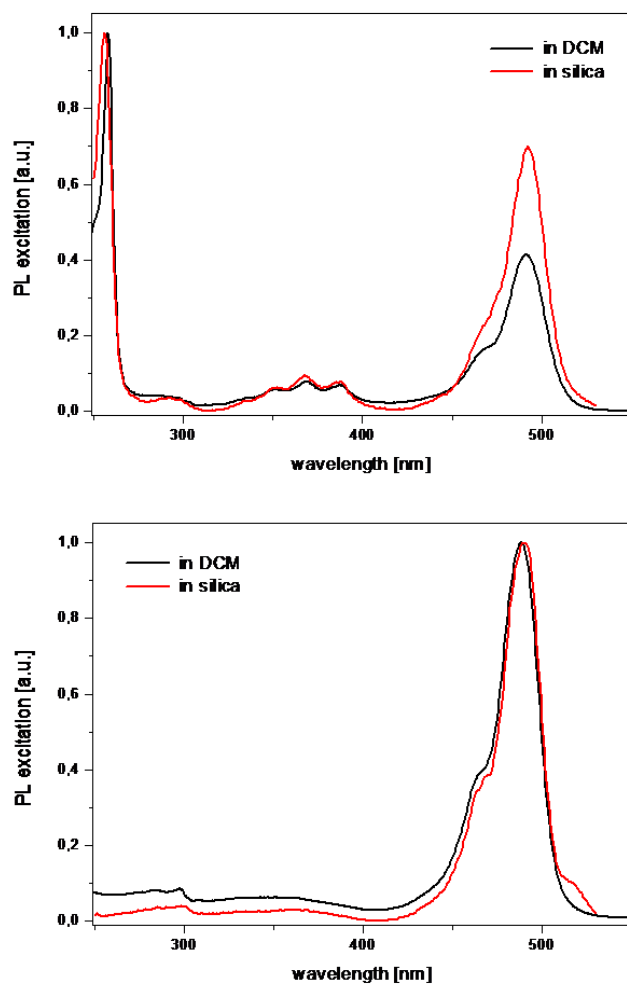
## Supporting Figures

### SAXS profiles and TEM



**Figure S7.** Left: SAXS profiles of the dye-loaded silica materials, as compared with standard COK-12 silica. Right: TEM micrograph of plain COK-12 silica particles, for comparison with 1S and 2S (Figure 2 in the paper).

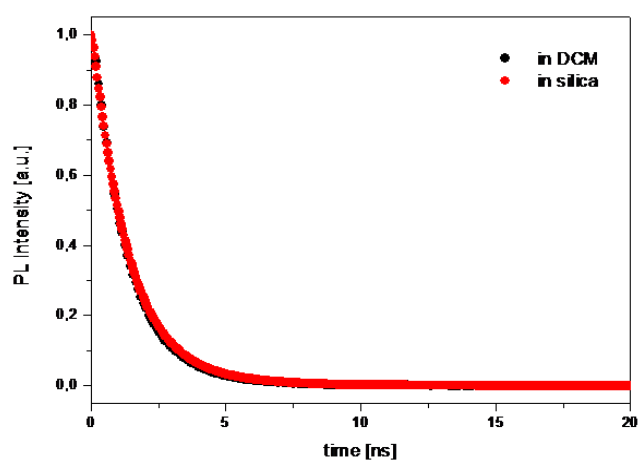
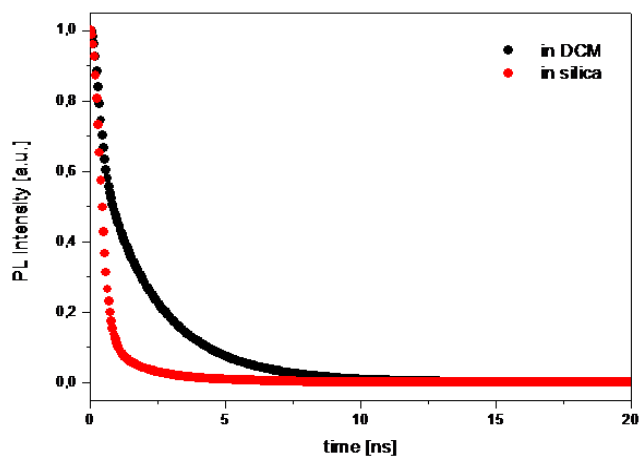
### Excitation spectra



**Figure S8.** Excitation spectra of the complexes **1** (top) and **2** (bottom) from  $4 \times 10^{-6}$  M dichloromethane solutions (black lines), compared with equimolar suspensions of the host-guest silica samples in water (red lines). All spectra were recorded at  $\lambda_{em} = 550$  nm, with both excitation and emission slits at 5 nm.

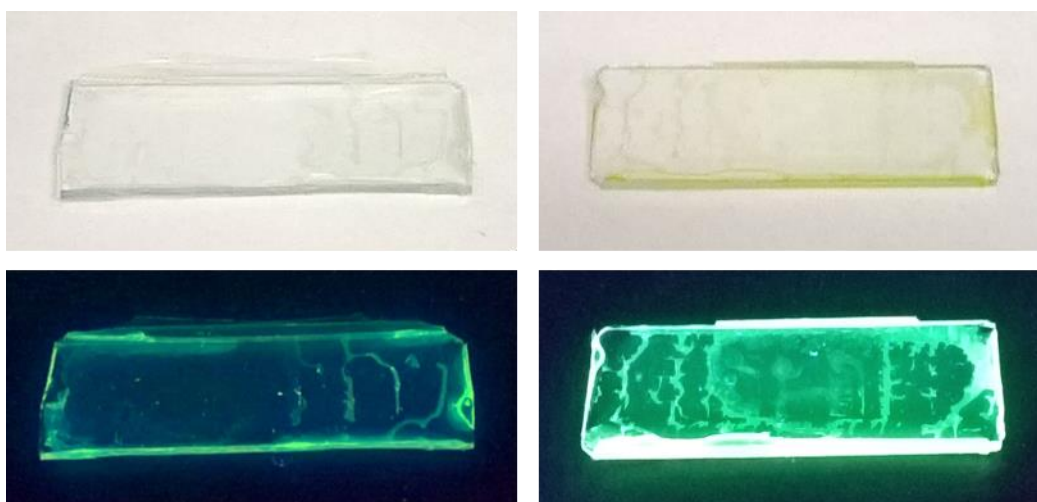
### Excited state decay profiles





**Figure S9.** Excited state decay profiles of the complexes **1** (top) and **2** (bottom) from  $4 \times 10^{-6}$  M dichloromethane solutions (black lines), compared to the profiles recorded from equimolar water suspensions of **1S** and **2S** (red lines), all measured at 530 nm under laser excitation at 472 nm.

### Films



**Figure S10.** Photographs of the **2**-doped (left) and the **2S**-doped PMMA films (right), under room light (top pictures) and under UV light (bottom pictures).

## Film preparation

Polymethyl metacrylate (PMMA) films with an average thickness of 3 mm were prepared according to the following procedures:

- a control film containing the polymer only was made by dissolving 45 mg of PMMA in 5 ml of HPLC grade toluene, followed by slow solvent evaporation until the solution was reduced to 2 ml; the solution was then dropcasted onto a microscopy glass slide (1 x 4 cm<sup>2</sup>) inserted into a Teflon support of matching size and left to dry at room temperature.
- the polymer film containing the free complex **2** was made by dissolving 45 mg of PMMA in 5 ml of HPLC grade toluene, to which were added 10 µl of a dichloromethane solution of **2** (1 mg / 10 ml); the solution was left stirring and allowed to reduce to 2 ml and the following steps were carried out as above.
- the polymer film containing the **2S** particles was made by dissolving 45 mg of PMMA in 5 ml of HPLC grade toluene, to which were added 0.9 mg of **2S**, corresponding to an equimolar amount of **2** in respect with the film containing the free complex; the subsequent steps followed the same route as above.