# **Supporting Information**

# Fluorescence quenching in Zn<sup>2+</sup> *bis*-terpyridine coordination polymers.

A single molecule study.

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Time-resolved emission spectroscopy in dilute solutions:

Figure S1: Time-resolved emission spectra of the free *bis*-terpyridine ligand (a,c) and the respective Zn<sup>2+</sup>-coordination polymer (b,d) in dilute DMF solutions. The transients in panel c and d show that the emission decays exponentially without any wavelength dependence. The errors in emission lifetime are in the sub-%-range of the lifetime. Panel e shows the steady-state emission spectra of the free *bis*-terpyridine ligand (green) and the respective Zn<sup>2+</sup>-coordination polymer (red), reconstructed by integrating the intensity in the experimental window.

## Sample preparation:

As mentioned in the main text a tailor made PMMA/PMA copolymer was used as matrix system. The purity of this matrix under typical SMS conditions was proofed by the acquisition of fluorescence images from pure matrix films. Figure S2 a shows such an image and visualizes the low background level which originates from the used matrix. Figure S2 b shows the fluorescence image of a typical sample, which was processed from highly diluted Zn<sup>2+</sup>-coordination polymer solution in freshly distilled DMF with a PMMA/PMA-matrix content of 10 mg/ml. Every bright spot represents an isolated single object. Figure S2 c shows a similar sample where pure PMMA was used as matrix. The polycationic character of the Zn<sup>2+</sup>-coordination polymer causes unmixing from the matrix during spin coating. This is nicely visualized by the occurrence of clusters. Figure S2 d shows a true colour image of a SMS sample prepared like the one depicted in Figure S2b. This image was acquired with a conventional digital camera. Most of the spots have a cyan colour, what is in good agreement with the emission spectra. The very few yellow spots are either aggregates or impurities.



Figure S2: Widefield fluorescence images of SMS-samples, prepared and measured in a different way. The white scale bar in each image is 18 μm in size. Panel a depicts the background under experimental condition while panel b and c show Zn<sup>2+</sup>-bis-terpyridine coordination polymer molecules in a PMMA/PMA (b) and a PMMA matrix (c). Panel shows an image from a similar sample like in panel b, recorded with a conventional digital camera.

# Extraction of the single molecules brightness from experimental data:

The values, necessary to calculate the brightness of a single object, were extracted from the fluorescence images using Brightstat. This is a program, which was made and optimized for this purpose and described in detail in previous publications by Scheblykin et al. (Oleg Mirzov, freeware, https://github.com/mirzov/BrightStat). The software identifies single objects and calculates its background corrected intensity and the excitation power at this particular position, which are used for tha calculation of the experimental brightness. Several quality criterias must be fulfilled that a bright spot is detected as a single molecule, e.g., a gaussian intensity profile with no other bright objects/pixels in a defined radius.



Figure S3: Figure S3 visualizes the afore mentioned quality criterias. The intensity of the yellow pixels has to follow a Gaussian distribution, while the smoothing radius (green circle), which is used for individual background correction, has to be free of any bright spot.

Using Brightstat it is possible to extract the information from a huge number of images, which is fundamental for statistics like brightness distribution.



### Excitation-power dependence of the experimental brightness:

Figure S4: Dependence of the average emission intensity of an ensemble of coordination polymers in a PMMA/PMA matrix on the excitation power. The green vertical line indicates the excitation power used in the experiments to determine the brightness of the polymers.

# Characterization of film properties by profiliometry:



Figure S5: Three dimensional image of a typical polymer film. The film was processed by spin coating of a DMF solution with 10 mg/mL PMMA/PMA matrix polymer onto freshly cleaned glass. The thickness of the film was measured to 35 nm.

### Emission spectroscopy at 77K:

In most cases, triplet states are non-emissive at room temperature. However, their phosphorescence can be observed at low temperatures. Therefore, the ligand as well as the polymer were investigated by steady-state emission spectroscopy at 77K. Figure S6 compares the experimental emission and excitation spectra recorded at low temperatures.



Figure S6: Emission spectra (solid lines) and excitation spectra (dashed lines) of the free *bis*terpyridine ligand (red) and the respective Zn<sup>2+</sup>-coordination polymer (green) recorded at 77 K.

From the direct comparison of the ligand and polymer emission spectra recorded at 77 K it is evident that the spectra are quite similar to the respective room temperature spectra. However, a shoulder is observable at around 600 nm in the case of the polymer. The spectra can be deconvoluted into two individual spectra with rather the same vibronic fine-structure, which is depicted in Figure S5.



Figure S7: Deconvolution of the 77K emission spectra of the  $Zn^{2+}$ -coordination polymer into two separate spectral contributions, which show similar vibronic progressions and are shifted by 3550 cm<sup>-1</sup> with respect to each other. The dashed component is assigned to S<sub>1</sub> fluorescence while the T<sub>1</sub> luminescence is shown with a dash-dotted line.

The similar vibronic fine-structure and the energy difference between both spectra hints to the fact that the less intense spectrum peaking at around 600 nm is due to phosphorescence from the  $T_1$ . The  $T_1$  has a more significant effect on the excited-state relaxation in the  $Zn^{2+}$ -coordination polymer compared to the relaxation in the ligand itself. This can be deduced from its contribution to the 77K emission spectrum. In the case of the ligand such contribution of  $T_1$  emission is not observed.