Electronic Supplementary Material (ESI) for RSC Advances.

Tunable Nanothermometer Based on Short Poly (phenylene ethynylene)

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This section includes:

- **Figure S1.** Fluorescence emission of PPE-CO_2-7 upon addition of incremental amounts of PVP of different molecular weights (10K, 55K, and 360K) at 20.0 ^oC.
- **Figure S2.** Emission spectra of PPE-CO_2-7 upon incremental addition of PVP 10K and 360K at 70.0 ^oC.
- **Figure S3**. Quenching experiment of PPE-CO_2-7 complexed with different PVP molecular weights (10K, 55K, and 360K) using methyl viologen (MV^{2+}) as the quencher at 70.0^oC.
- **Figure S4**. Thermal response of PPE-CO_2-7 complexed with 360K PVP between 10^oC and 90^oC.
- **Figure S5**. Fluorescence emission spectrum of PPE-CO2-7 in complexation with (A) 10K, (B) 55K, and (C) 360K PVP acquired at different temperatures between 15.0 °C and 70.0 °C with a 5.0 °C increment.
- **Figure S6:** Time response of PPE-CO_2-7 complexed with 10K, 55K, and 360K PVP upon changing the temperature from 20.0 ^oC to 55.0 ^oC.
- **Figure S7:** Thermal response of PPE-CO_2-7 in complexation with PVP 360K prepared in 10 mM HEPES and 150mM NaCl at (A) pH=5 and (B) 11.
- **Figure S8:** Thermal response of PPE-CO_2-7 in complexation with 10K and 55K PVP prepared in 10 mM HEPES and 30 mM $CaCl_2$ and pH = 7.

Radius of Gyration and Hydrodynamic Critical Concentrations:

The radii of Gyration of the different PVP molecular weights were calculated using the equation below:

$$R_g = A \times M_w^b$$

Where A=0.927 and b=0.621 as determined by Bartoszek *et al.* by fitting previously reported data.[1]

The hydrodynamic critical concentrations were estimated for the three molecular weighs using the formula below:[2]

$$C^* = \frac{3M}{4\pi N_A R_g^3}$$

In our calculation, we assumed $M=M_w$.

Fluorescence titration:

To tune the probe sensitivity and the interaction between PPE-CO_2-7 and PVP, increasing concentrations of PVP were added to a solution of PPE-CO_2-7 at 20.0 °C and 70.0 °C. At 20.0 °C, the fluorescence emission of the aggregated CPEs increased with the addition of PVP. At higher concentrations, a new peak reflecting the destabilized state appeared at 485 nm. Higher PVP molecular weights exhibited a capability to better dissolve individual polymer chains (Figure S1). At 70.0 °C, the CPE emission that started at 485 nm quickly shifted to 450 nm (Figure S2). Upon increasing the PVP concentration, the fluorescence emission increased as a result of more dissolved PPE-CO_2-7.

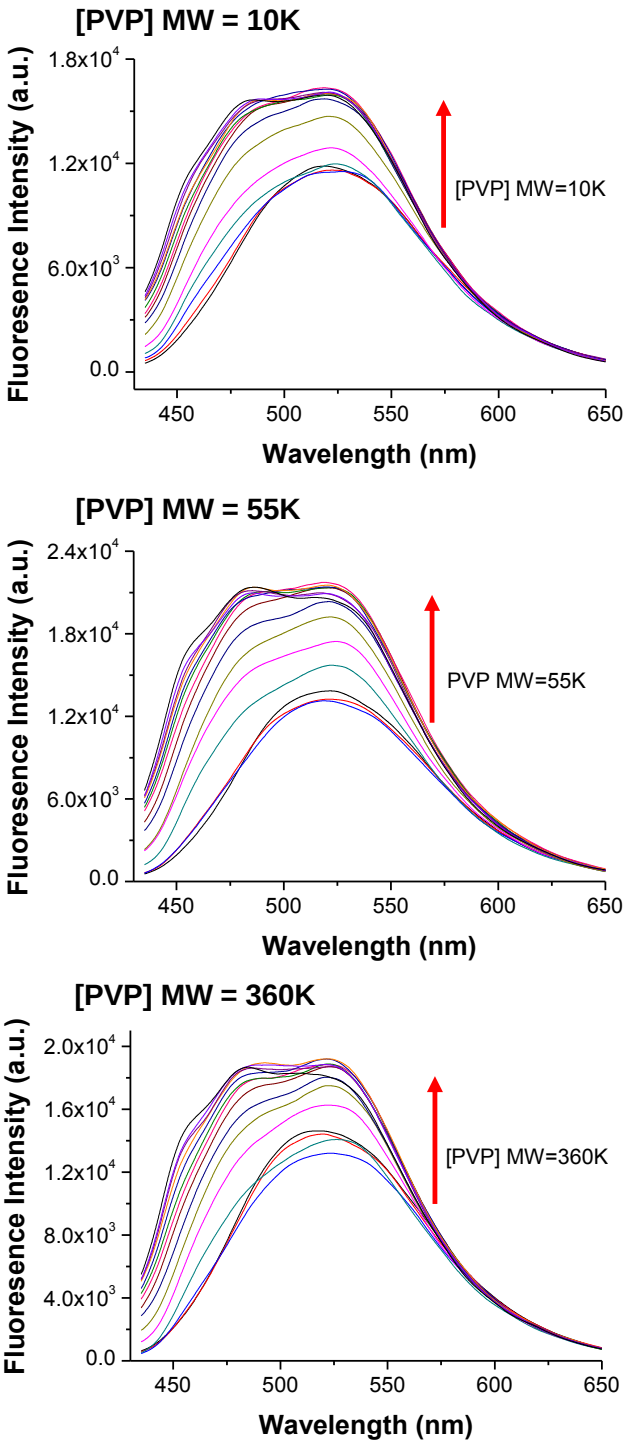

Figure S1: Fluorescence emission of PPE-CO_2-7 upon addition of incremental amounts of PVP of different molecular weights (10K, 55K, and 360K) at 20.0 ^{o}C.

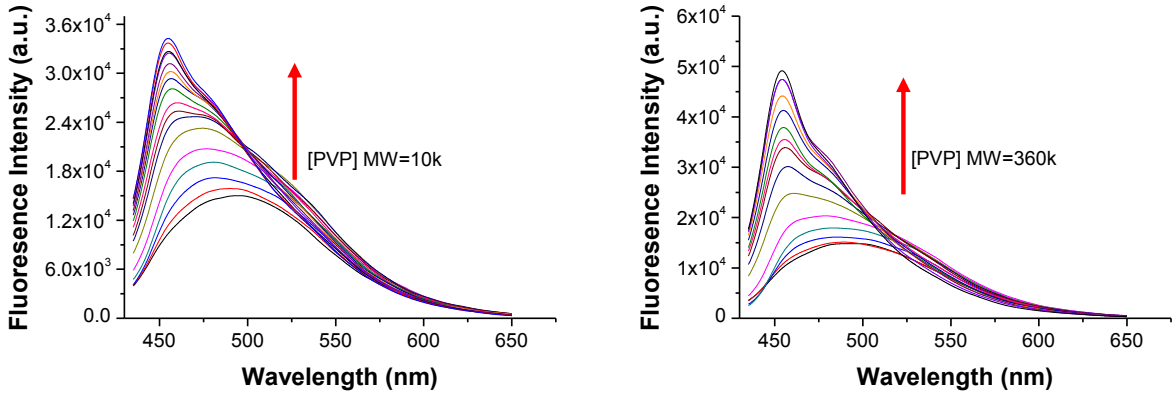

Figure S2: Emission spectra of PPE-CO_2-7 upon incremental addition of PVP 10K and 360K at 70.0 ^oC.

Fluorescence Quenching:

To further understand the interaction between PPE-CO_2-7 and PVP, a series of quenching experiments were conducted at 20.0 ^oC and 70.0 ^oC using methyl viologen (MV^{2+}) as the quencher. MV^{2+} with different concentrations was added incrementally, and the emission intensity of PPE-CO_2-7 was measured after each addition. The emission intensities were efficiently reduced by methyl viologen. However, the emission intensity of PPE-CO_2-7 complexes with low PVP molecular weights (10K and 55K) at around 520 nm was greater than the emission intensity with higher PVP molecular weight (360K). This indicates that the number of remaining PPE-CO_2-7 aggregated species with lower PVP molecular weight is greater than the remaining aggregated species with 360K (Figure S3).

In addition, the initial intensity of PPE-CO_2-7 complexed with 360K PVP is almost double the initial intensity of PPE-CO_2-7 complexed with either 10K or 55K. This indicates that 360K PVP is capable of disaggregating higher amount of PPE-CO_2-7 than the other PVP MWs, and hence a larger amount is being dissolved.

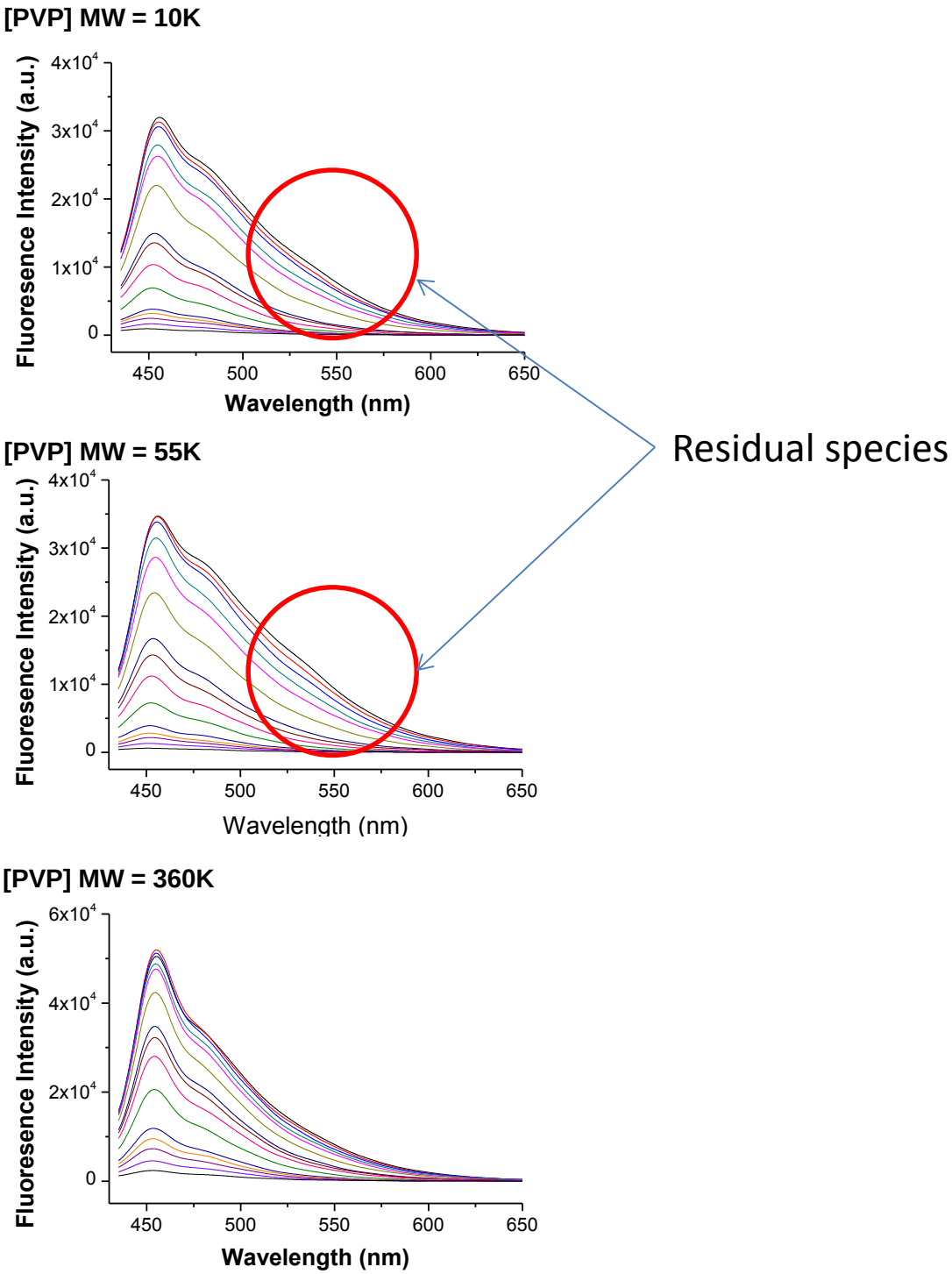

Figure S3: Quenching experiment of PPE-CO_2-7 complexed with different PVP molecular weights (10K, 55K, and 360K) using methyl viologen (MV^{2+}) as the quencher at 70.0°C.

Temperature sensing:

PPE-CO_2-7 with a final concentration of 5 μg.mL^{-1} prepared in 10 mM HEPES and 150 mM NaCl buffer solution (pH=7.3) was complexed with PVP (10K, 55K, or 360K) at a final concentration of 2.5 mg.mL^{-1}, unless otherwise stated. Temperature controlled experiments were

performed using a T3 Quantum Northwest unit. To maintain a homogenous temperature, the solution was continuously stirred. Before each measurement solution was allowed to stabilize for 2 to 3 minutes. Each experiment was done in at least three replicates (Figure S5).

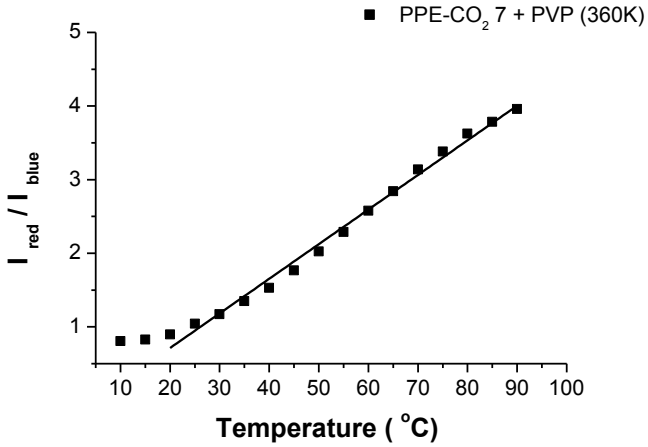

Figure S4: Thermal response of PPE-CO_2-7 in complexation with 360K PVP between 10.0 ^{o}C and 90.0 ^{o}C.

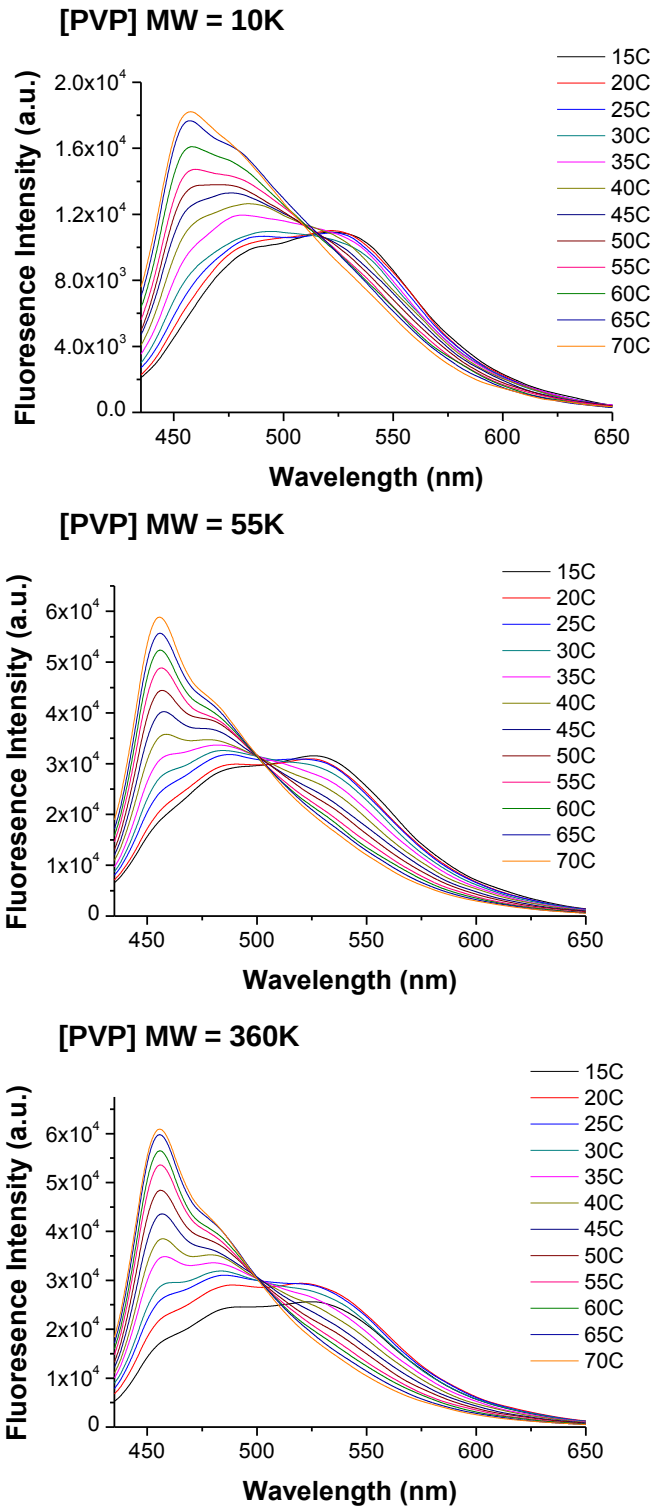

Figure S5: Fluorescence emission spectrum of PPE-CO_2-7 in complexation with (A) 10K, (B) 55K, and (C) 360K PVP acquired at different temperatures between 15.0 °C and 70.0 °C with a 5.0 °C increment.

Response Time:

To probe the response time, three solutions each prepared with a different PVP MW was stepped from 20.0 °C to 55.0 °C. The three solutions showed a correlated response rate between the fluorescent intensity and the temperature changes as evident by the calculated slope of the initial intensity (Figure S6).

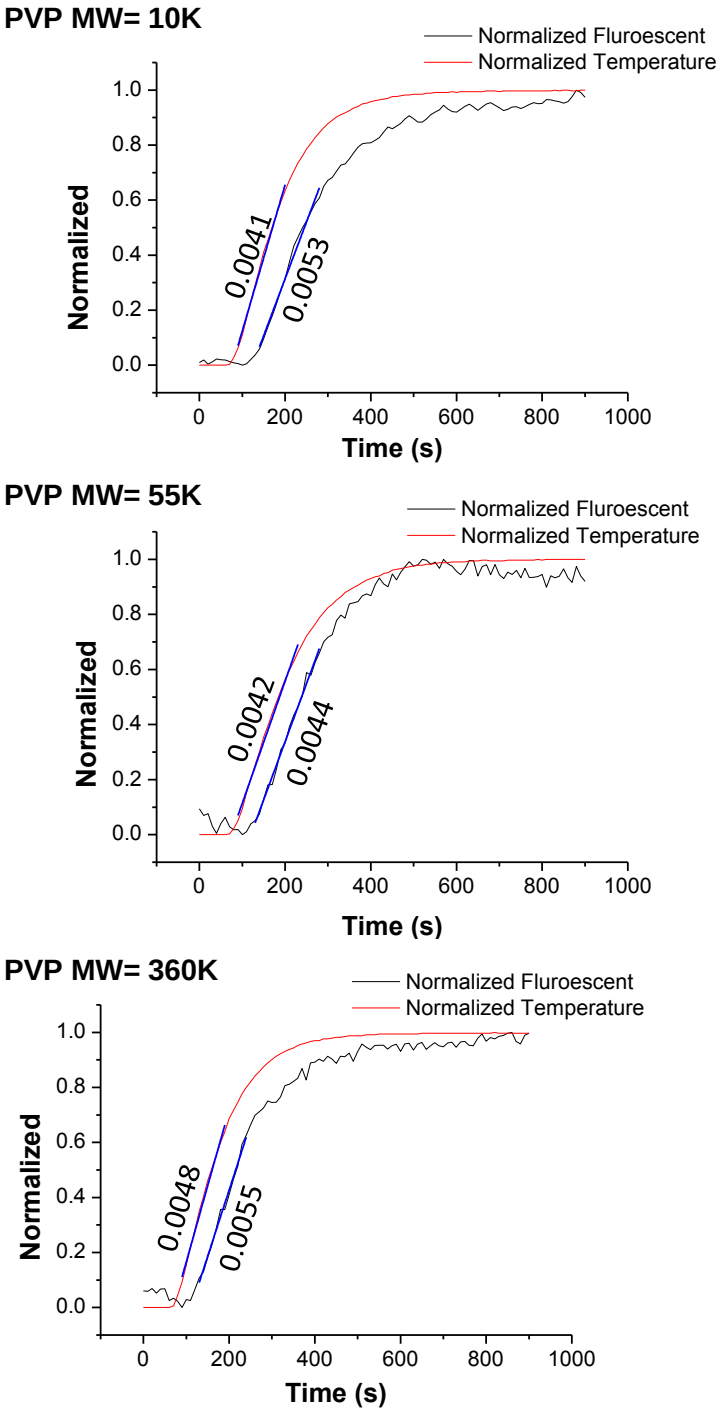

Figure S6: Time response of 5 μg.mL^{-1} PPE-CO_2-7 complexed with 2.5 mg.mL^{-1} of 10K, 55K, and 360K PVP respectively upon changing the temperature from 20.0 °C to 55.0 °C. Values on the graph represent the calculated slopes for the fitted region highlighted in blue.

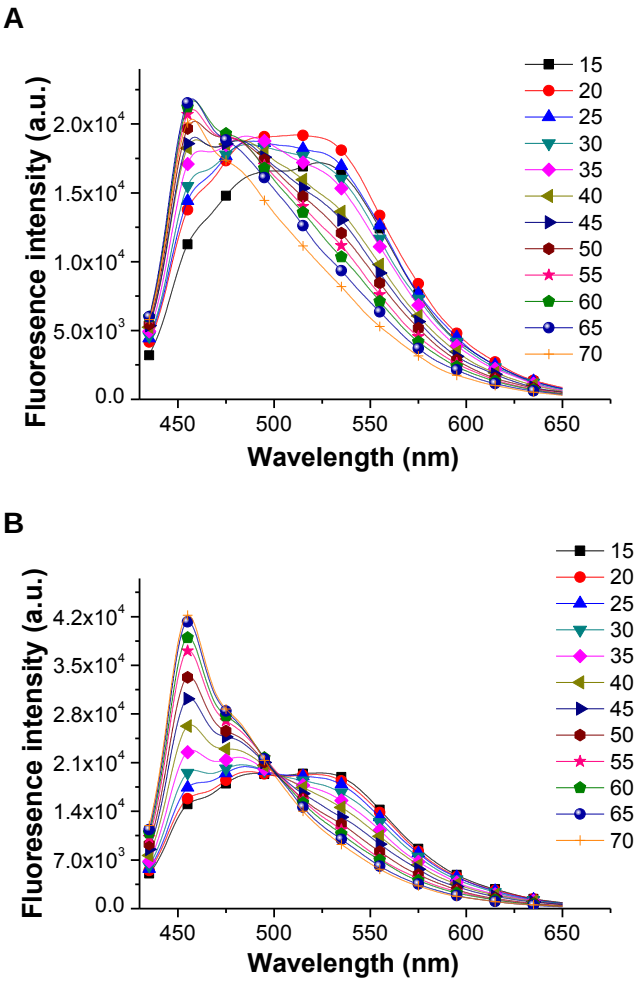

Figure S7: Thermal response of PPE-CO_2-7 in complexation with PVP 360K prepared in 10 mM HEPES and 150 mM NaCl at (A) pH = 5 and (B) pH = 11.

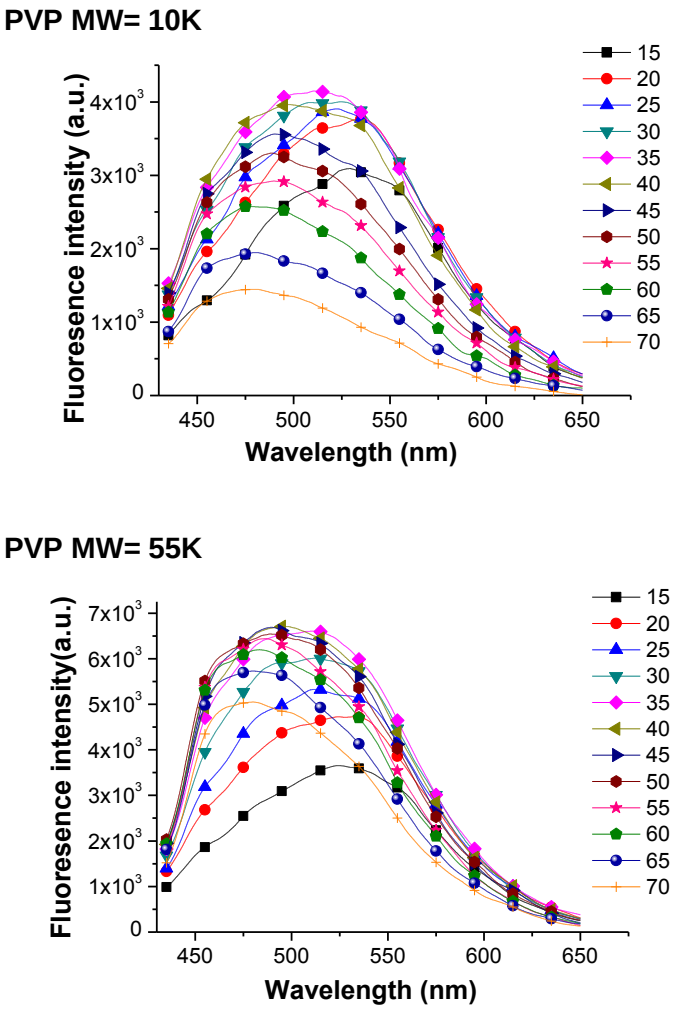

Figure S8: Thermal response of PPE-CO_2-7 in complexation with 10K and 55K PVP prepared in 10 mM HEPES and 30 mM $CaCl_2$ and pH = 7.

References:

1. N. Bartoszek, P. Ulański and J. M. Rosiak, *International Journal of Chemical Kinetics*, 2011, **43**, 474-481.
2. I. Teraoka, *Frontmatter and Index*, Wiley Online Library, 2002.