Electronic Supplementary Material (ESI) for RSC Advances.

Optical spectroscopic studies on the complexation of stilbazolium dyes with a water soluble pillar[5]arene

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Electronic Supporting Information (ESI)

1. Materials and methods

Solvents, reagents and starting materials were obtained from commercial supplier and used without further purification. **WPA5**, **G1**-**G3** were prepared as described before (Ref. 16-17). **DMV** diiodide salt was used. All the spectroscopic experiments were carried out at 25°C. The UV−vis absorption spectra were recorded on an Agilent 8453 diode array spectrometer. The steady-state fluorescence spectra and fluorescence decay curves were measured on an Edinburgh Instruments FLSP 920 combined steady-state and lifetime spectrometer, which uses the method of time-correlated single-photon counting for measuring the fluorescence decay. The excitation light source was a Xe900 steady state arc lamp when measuring the fluorescence spectra and an EPL 375 pulsed diode laser when the fluorescence decay curves were recorded. This diode laser emitted pulses of 130 ps fwhm (full width at half-maximum) at 378 nm. The fluorescence quantum yields of **G3** and its complex with **WPA5** were determined using cresyl violet as standard. ^{1}H NMR spectra were taken on a Bruker Avance DRX-500 spectrometer with chemical shifts reported in ppm (the residual DMSO was used as internal standard).

*2. Absorption and fluorescence spectra of **G1**-**WPA5** and **G2**- **WPA5**systems*

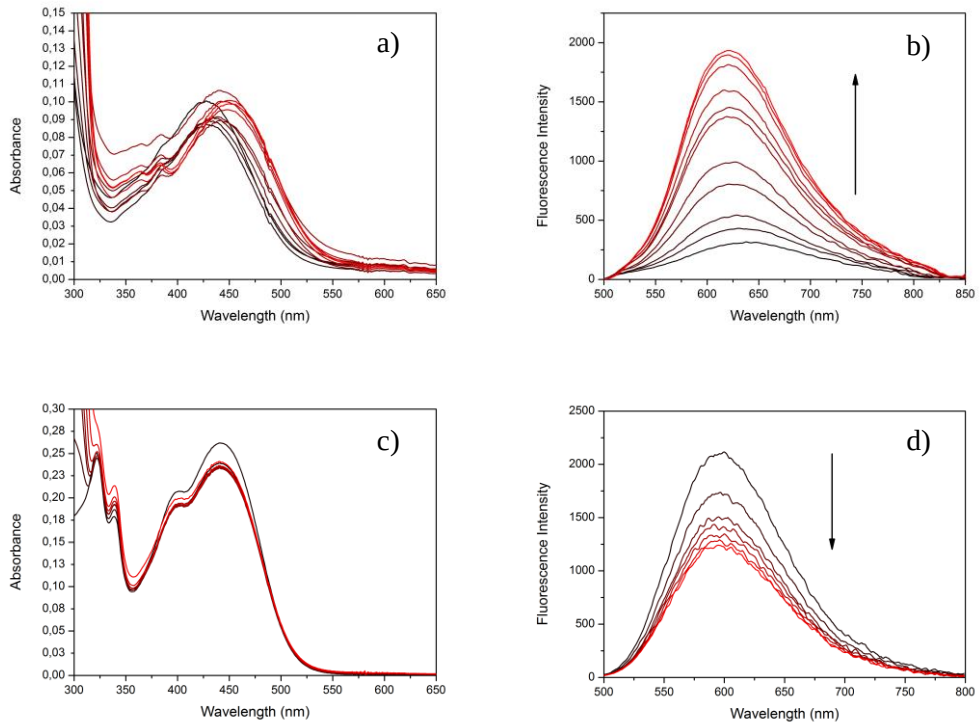

Fig. S1 Absorption(**a**) and fluorescence spectra (**b**) of **G1** (10.0 μM) upon addition of **WPA5** (0 to 3.92 equiv.) in water (excitation at 429 nm); absorption (**c**) and fluorescence (**d**) spectra of **G2** (10.0 μM) upon addition of **WPA5** (0 to 15.2 equiv.) in water-ethanol 1:1 mixture (excitation at 441 nm), K_1 = $(2.64\pm0.2)\cdot10^5$ M^{-1}. *Note: due to E/Z photoisomerism of **G1**, the spectral data were not suitable for the determination of the association constant.*

*3. Job's plots of **G2-WPA5** and **G3- WPA5** systems*

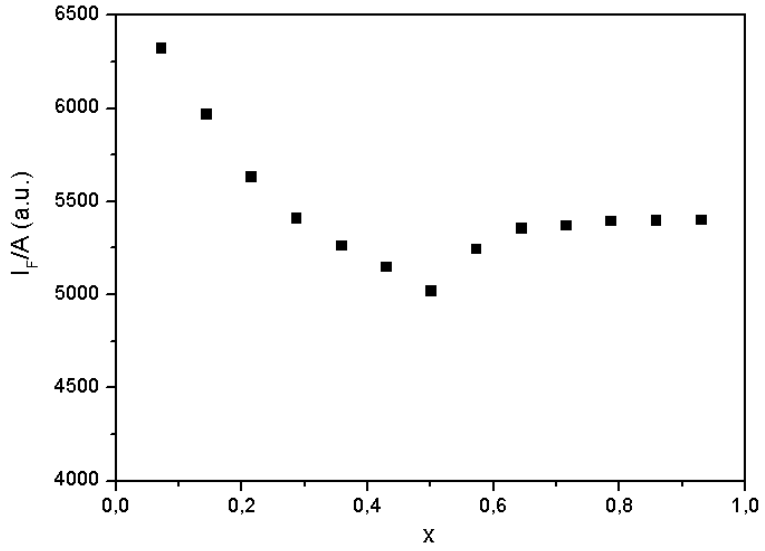

Fig. S2. Job's plot of the fluorescence intensity / absorbance data of **G2-WPA5** systems in water-ethanol 1:1 solvent mixtures, λ_{em} = 595 nm, λ_{ex} = 445 nm. The sum of the total concentrations, *x*, was 10 μM, to achieve a detectable complex formation. The self-absorption of samples with higher dye concentrations was strong, causing a distortion of the triangle-shaped plot.

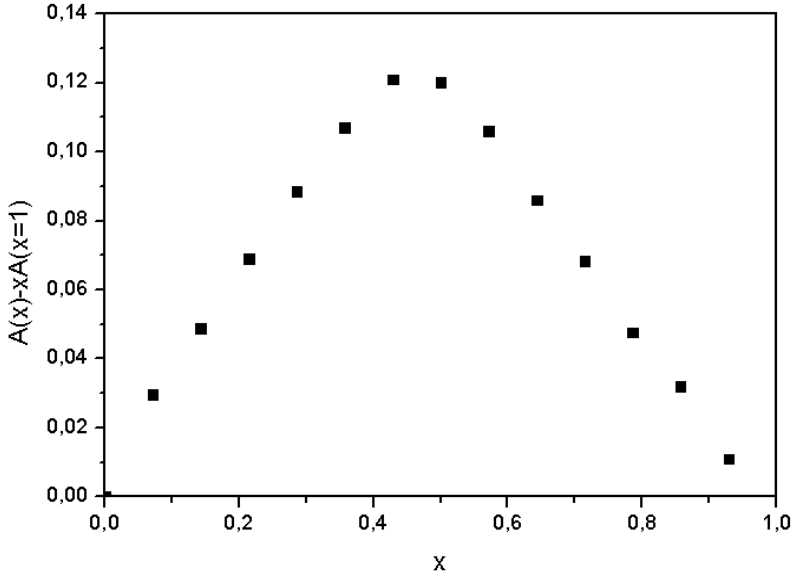

Fig. S3 Modified Job's plot [S1] of the *A*(*x*) absorbance values of **G3 - WPA5** mixturesin aqueous solutions, measured at λ =537 nm. *x* denotes the mole fraction of **G3**, *A*(*x*=1) is the absorbance of the pure dye. The sum of the total concentrations is 50.0 μM.

4. Association constant determination

The 1:1 stoichiometries of the **G2·WPA5** and **G3·WPA5** complexes were justified by Job's method (see Figs. S2 and S3). As the absorption spectrum of **G2** showed only minor changes when **WPA5** was added to its solution (see Fig S1c), the association constant K_1 for the complex was determined from the fluorescence spectra of solutions with constant **G2** and different **WPA5** concentrations. The calculation is described at the end of this section.

The association constant, K_1, and the spectrum of the **G3·WPA5** complex were obtained from the absorption spectra of the free dye and of **G3-WPA5** mixtures with identical **G3**, but different **WPA5** total concentrations. For that the equilibrium concentrations of the their complex, c_j^{HG}, in the *j*-th solution were expressed from the equations

$$c_j^{HG} / \left(c_j^H c_j^G\right) = K_1, \tag{S1}$$

$$c_j^G + c_j^{HG} = c_0^G, \tag{S2}$$

and

$$c_j^H + c_j^{HG} = c_{0j}^H, \tag{S3}$$

(c_0^G and c_{0j}^H are the total concentrations). The second order equation

$$K_1\left(c_j^G\right)^2 - \left(K_1 c_0^G + K_1 c_{0j}^H + 1\right)c_j^G + K_1 c_0^G c_{0j}^H = 0 \tag{S4}$$

was obtained, the root of which was substituted into the sum of squared residuals

$$S_{tot}^{abs} = \sum_{i=1}^{n}\sum_{j=1}^{m}\left[A_{i,j} - \varepsilon_i^{HG} c_j^{HG} - \varepsilon_i^G\left(c_0^G - c_j^{HG}\right)\right]^2. \tag{S5}$$

In Eq. (S5) $A_{i,j}$ is the measured absorbance, ε_i^G and ε_i^{HG} are the absorption coefficients of the respective species at the *i*-th wavelength. S_{tot}^{abs} has been minimized as a function of ε_i^{HG}-s and K_1. This optimization yielded K_1 = 1.3×10^6 M^{-1}, and the absorption spectrum of **WPA5·G3** complex. The latter is shown in Fig. S4, together with the spectrum of the uncomplexed dye.

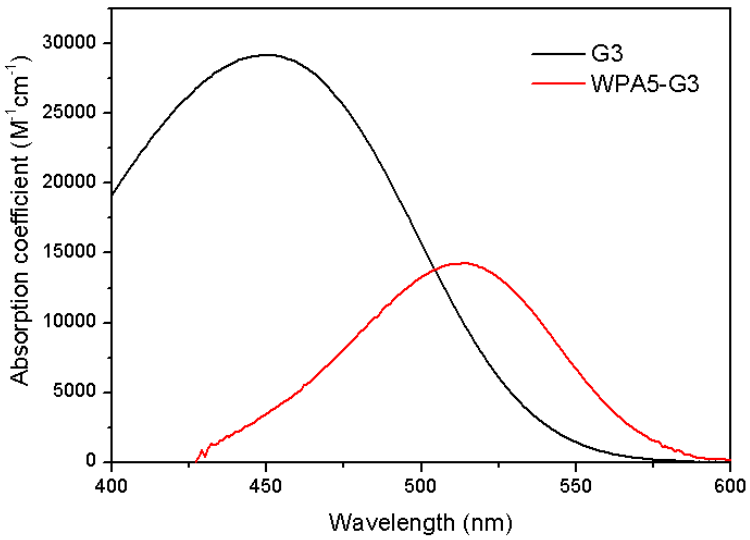

Fig. S4. The absorption spectrum of the **WPA5·G3** complex and the uncomplexed G3 dye.

The equilibrium constant K_2 for the binding of the viologen V by the pilllarene host H, has been determined from the spectra of solutions with identical dye total concentrations and identical pillararene concentrations, but with different viologen concentrations.

In the presence of the viologen, V, which forms the complex HV with the pillarene host, the equilibrium concentration of the dye complex in the j-th solution, c_j^{HG}, can be expressed from the two equilibrium constants, (S1) and

$$c_j^{HG} / \left(c_j^H c_j^V \right) = K_2 , \qquad \text{(S6)}$$

and from the expressions for the total concentrations (S2),

$$c_j^V + c_j^{HV} = c_{0j}^V , \qquad \text{(S7)}$$

and

$$c_j^H + c_j^{HG} + c_j^{HV} = c_0^H . \qquad \text{(S8)}$$

For the equilibrium concentrations of the dye complex in the individual solutions a cubic equation was derived:

$$\left(K_1 K_2 - K_1^2 \right) \left(c_j^G \right)^3 + \left[\left(2K_1^2 - K_1 K_2 \right) \left(c_0^G + c_{0j}^V \right) + \left(2K_1^2 - K_1 K_2 \right) c_0^G + K_1 K_2 c_{0j}^V + K_1 - K_2 \right] \left(c_j^G \right)^2 -$$
$$- \left[\left(2K_1^2 - K_1 K_2 \right) c_0^H c_0^G + K_1 K_2 c_0^G c_{0j}^V + K_1 c_0^G + K_1^2 \left(c_0^G \right)^2 \right] c_j^G + K_1^2 \left(c_0^G \right)^2 c_0^H = 0. \qquad \text{(S9)}$$

The value of K_2 was obtained then by another least square fitting, applying Eq. (S5) for the spectra of the V-G-H systems, adopting the previously determined values for K_1 and the absorption coefficients ε_i^{HG}, and using Eq. (S9) for the calculation of c_j^{HG}.

The value of K_1 for **WPA5·G2** was determined from the fluorescence spectra. For that the spectra were divided by the absorbance at the excitation wavelength to compensate for the

difference of absorbance at the excitation wavelength at different host concentrations, have been corrected for the (small) inner filter effect and substituted into the sum of squared residuals

$$S_{tot}^{fl} = \sum_{i=1}^{n}\sum_{j=1}^{m}\left[I_{i,j} - \varphi_i^{HG} c_j^{HG} - \varphi_i^{G}\left(c_0^{G} - c_j^{HG}\right)\right]^2 \qquad \text{(S10)}$$

In eq (S10) $I_{i,j}$ denotes the corrected fluorescence intensity of the *j*-the mixture, φ_i^G and φ_i^{HG} denote the molar fluorescence intensities of the dye guest and the complex, respectively, at the *i*-th wavelength. Performing a minimization of S_{tot}^{fl} yielded $K_1 = (2.64\pm0.2)\cdot10^5\ M^{-1}$.

5. *NMR spectra of **G1**- **WPA5** system*

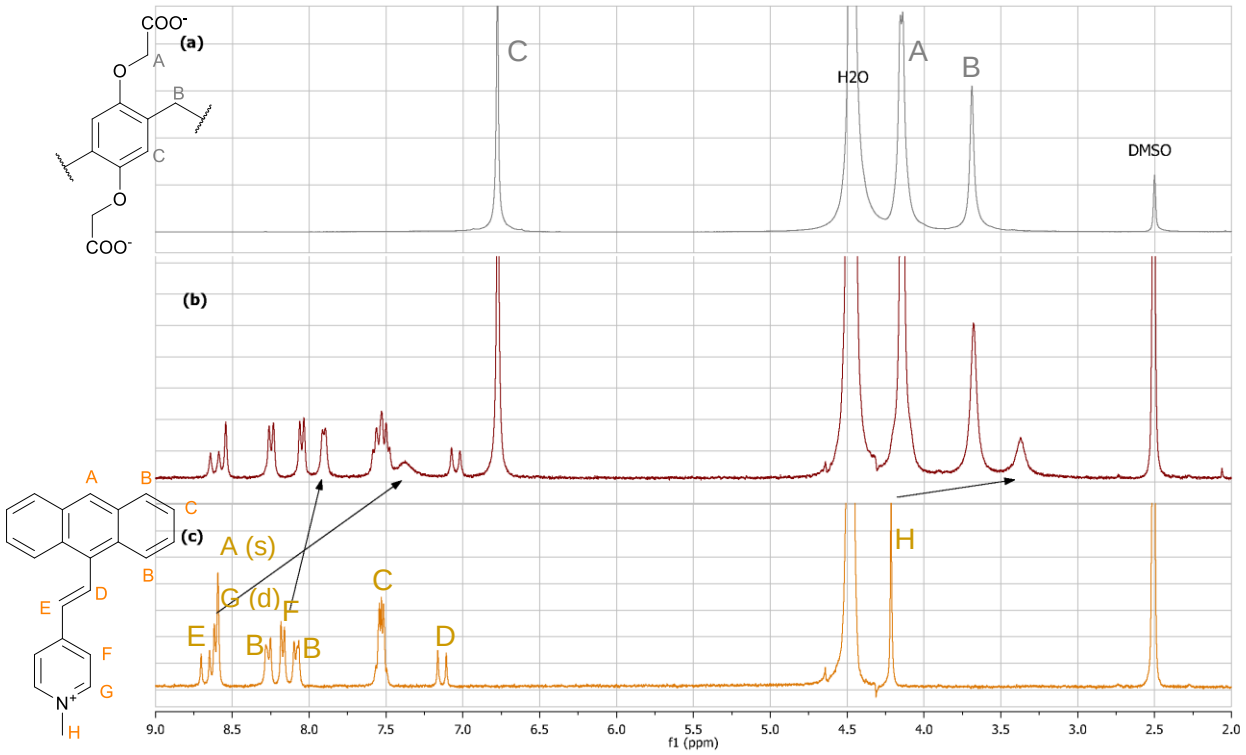

Fig. S5 Partial 1H-NMR spectra (500 MHz, D2O - DMSO-d6 1:1, 298 K) of (a**5**;) **WPA5** (b) **G1** and **WPA5** (1 equiv.), (c) **G3** *Note: the poor quality of the spectra is attributed to the low concentration due to the low solubility of **G1** in D_2O*

6. *Fluorescence decay of **WPA5·G3** complex*

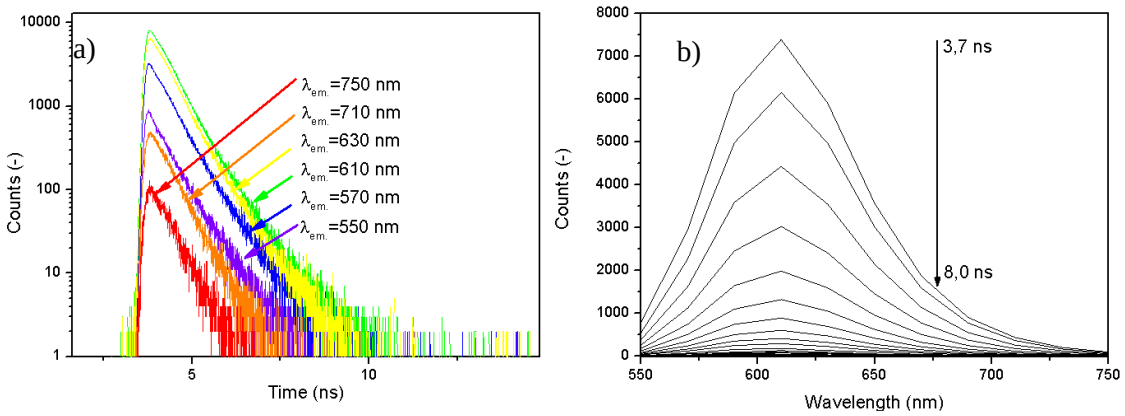

Fig. S6. (a) Fluorescence decay curves and (b) time-resolved emission spectra of a 5×10^{-6} M aqueous solution of **G3** in the presence of 1.5×10^{-5} M **WPA5**.

7. *Sensitivity of **G3·WPA5** fluorescence indicator displacement system*

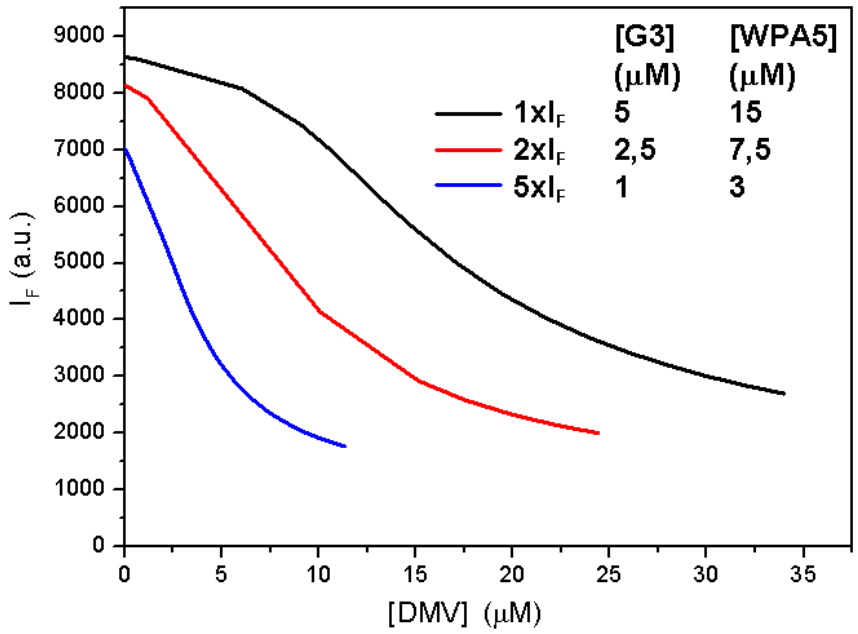

Fig. S7. Fluorescence intensities of **G3·WPA5** systems in the presence paraquat in various concentrations, as calculated from the association constants K_1 and K_2.

8. *References*

[S1] K. Hirose, *J. Incl. Phenom. Macrocycl. Chem.* 2001, **39** 193-202