# Supporting Information

## Supramolecular control of the photoisomerization of a coumarin based photoswitch

*Etelka Kiss [a], Dávid Mester [a,b,c], Márton Bojtár [d], Zsombor Miskolczy [e], László Biczók [e], Dóra Hessz [a], Mihály Kállay [a,b,c] and Miklós Kubinyi [a,*]*

[a] Department of Physical Chemistry and Materials Science, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, 1111, Budapest, Műegyetem rkp. 3, Hungary

[b] MTA-BME Lendület Quantum Chemistry Research Group, Budapest University of Technology and Economics, 1111, Budapest, Műegyetem rkp. 3, Hungary;

[c] ELKH-BME Quantum Chemistry Research Group, Budapest University of Technology and Economics, 1111, Budapest, Műegyetem rkp. 3, Hungary;

[d] Chemical Biology Research Group, Institute of Organic Chemistry, Research Centre for Natural Sciences, 1117, Budapest, Magyar Tudósok krt. 2, Hungary

[e] Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, HUN-REN Research Network, H-1519 Budapest, P.O. Box 286, Hungary

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[*] Corresponding author.
E-mail address: kubinyi.miklos@vbk.bme.hu (M. Kubinyi).

## S1. NMR spectra

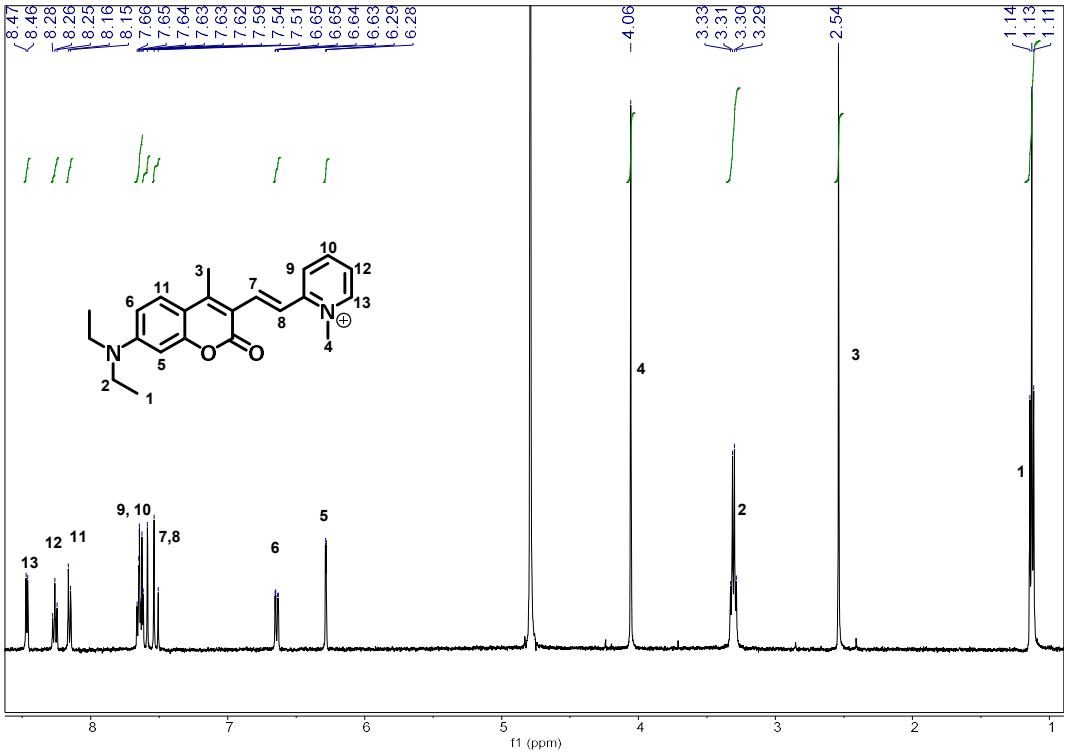


Fig. S1: $^{1}$H-NMR spectrum of *trans*-CP at 500 MHz, $D_2O$.

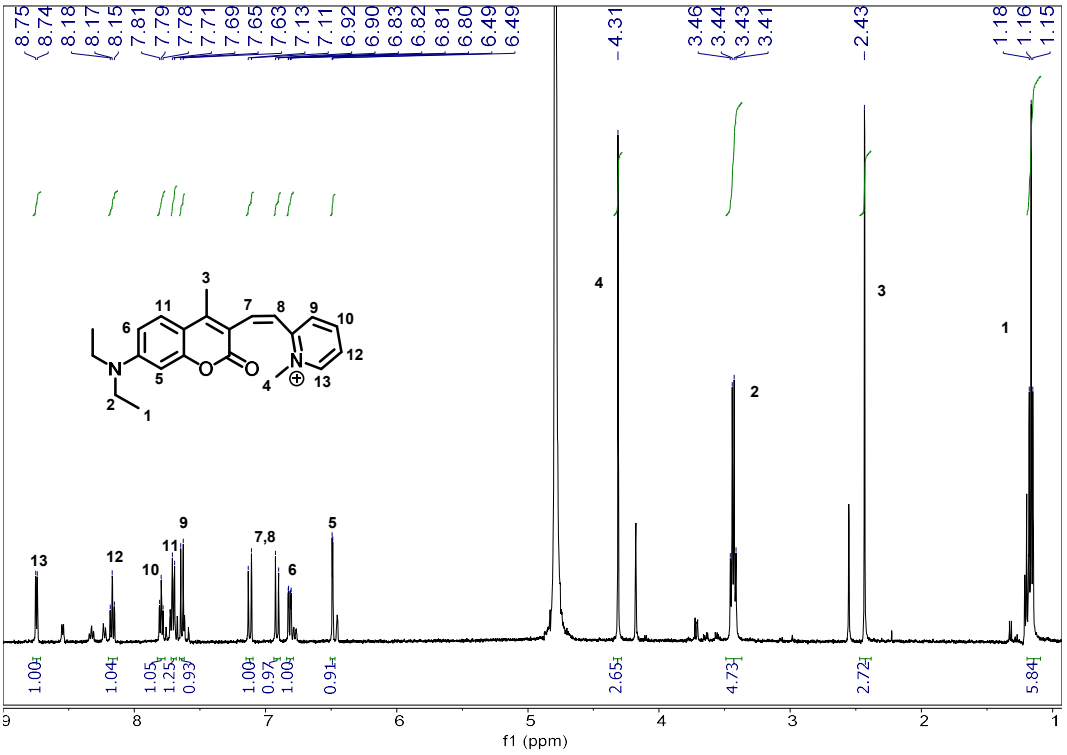


Fig. S2: $^{1}$H-NMR spectrum of a PSS containing 75% *cis*-CP at 500 MHz in $D_2O$

## S2. Photokinetic experiments

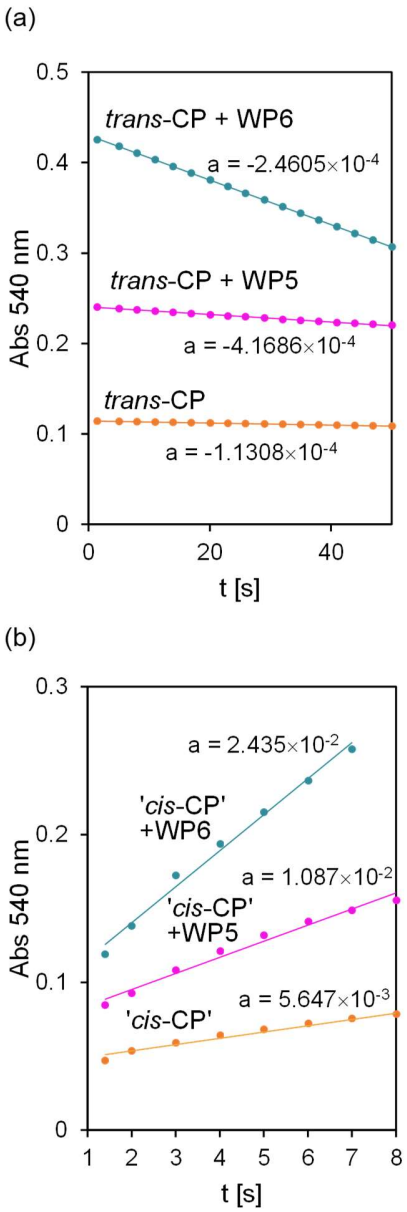


Fig. S3: Initial $A^D(t)$ data of (a) of *trans*-CP, and its mixture with WP5 and WP6, irradiated with the green (540 nm) LED; (b) a PSS system with 75% *cis*-CP and its mixtures with WP5 and WP6, irradiated with the UV (370 nm) LED. "a" is the slope of linearly fitted data ($s^{-1}$). Concentrations as given in the captions of Figs. 5 and 6.

## S3. Chemical shifts of the isomeric forms of CP in their WPn complexes

Table S1: Chemical shifts of *trans*-CP, *cis*-CP and their WP5 complexes

| | **WP5** | ***trans*-CP** | | ***'cis*-CP'** | |
|---|---|---|---|---|---|
| | *free* | *free* | *1 equiv. WP5* | *free* | *1 equiv. WP5* |
| **Proton** | *δ [ppm]* | *δ [ppm]* | | *δ [ppm]* | |
| A | 4.27 | | 4.16 | | 4.19 |
| B | 3.84 | | 3.78 | | 3.81 |
| C | 6.73 | | 6.64 | | 6.67 |
| 1 | | 1.20 | 1.09 | 1.16 | 0.97 |
| 2 | | 3.55 | 3.23 | 3.43 | 3.21 |
| 3 | | 2.55 | 2.39 | 2.43 | 2.36 |
| 4 | | 4.18 | 3.95 | 4.31 | 4.25 |
| 5 | | 6.28 | 6.15 | 6.49 | 6.35 |
| 6 | | 6.64 | 6.51 | 6.82 | 6.73 |
| 7 | | 7.52 | 7.38 | 6.91 | 6.83 |
| 8 | | 7.60 | 7.53 – 7.43 | 7.12 | 7.03 |
| 9 | | 7.68 – 7.62 | 7.53 – 7.43 | 7.70 | 7.64 |
| 10 | | 7.68 – 7.62 | 7.53 – 7.43 | 7.79 | 7.70 |
| 11 | | 8.16 | 8.05 | 7.64 | 7.56 – 7.46 |
| 12 | | 8.27 | 8.10 | 8.17 | 8.04 |
| 13 | | 8.47 | 8.31 | 8.75 | 8.66 |

Table S2: Chemical shifts of *trans*-CP, *cis*-CP and their WP6 complexes

| | **WP6** | ***trans*-CP** | | ***cis*-CP** | |
|---|---|---|---|---|---|
| | *free* | *free* | *1 equiv. WP6* | *free* | *1 equiv. WP6* |
| **Proton** | *δ [ppm]* | *δ [ppm]* | | *δ [ppm]* | |
| A | 4.07 | | 4.23 | | 4.27 |
| B | 3.86 | | 3.86 | | 3.87 |
| C | 6.64 | | 6.79 | | 6.82 |
| 1 | | 1.20 | 0.16 | 1.16 | – 0.15 |
| 2 | | 3.55 | 2.16 | 3.43 | 1.88 |
| 3 | | 2.55 | 2.49 | 2.43 | 2.24 |
| 4 | | 4.18 | 4.05 | 4.31 | 4.25 – 4.09 |
| 5 | | 6.28 | 5.58 | 6.49 | 5.61 |
| 6 | | 6.64 | ? | 6.82 | ? |
| 7/8 | | 7.52 | 7.09 | 6.91 | ? |
| 7/8 | | 7.67 – 7.61 | 7.62 – 7.42 | 7.12 | 7.13 |
| 9 | | 7.67 – 7.61 | 7.79 – 7.42 | 7.70 | 7.78 – 7.50 |
| 10 | | 7.67 – 7.61 | 7.79 – 7.42 | 7.79 | 7.78 – 7.50 |
| 11 | | 8.16 | 8.16 – 8.02 | 7.64 | 7.78 – 7.50 |
| 12 | | 8.27 | 8.16 – 8.02 | 8.17 | 8.08 |
| 13 | | 8.47 | 8.33 | 8.75 | 8.70 |

## S4. NMR spectra of the PSS mixtures

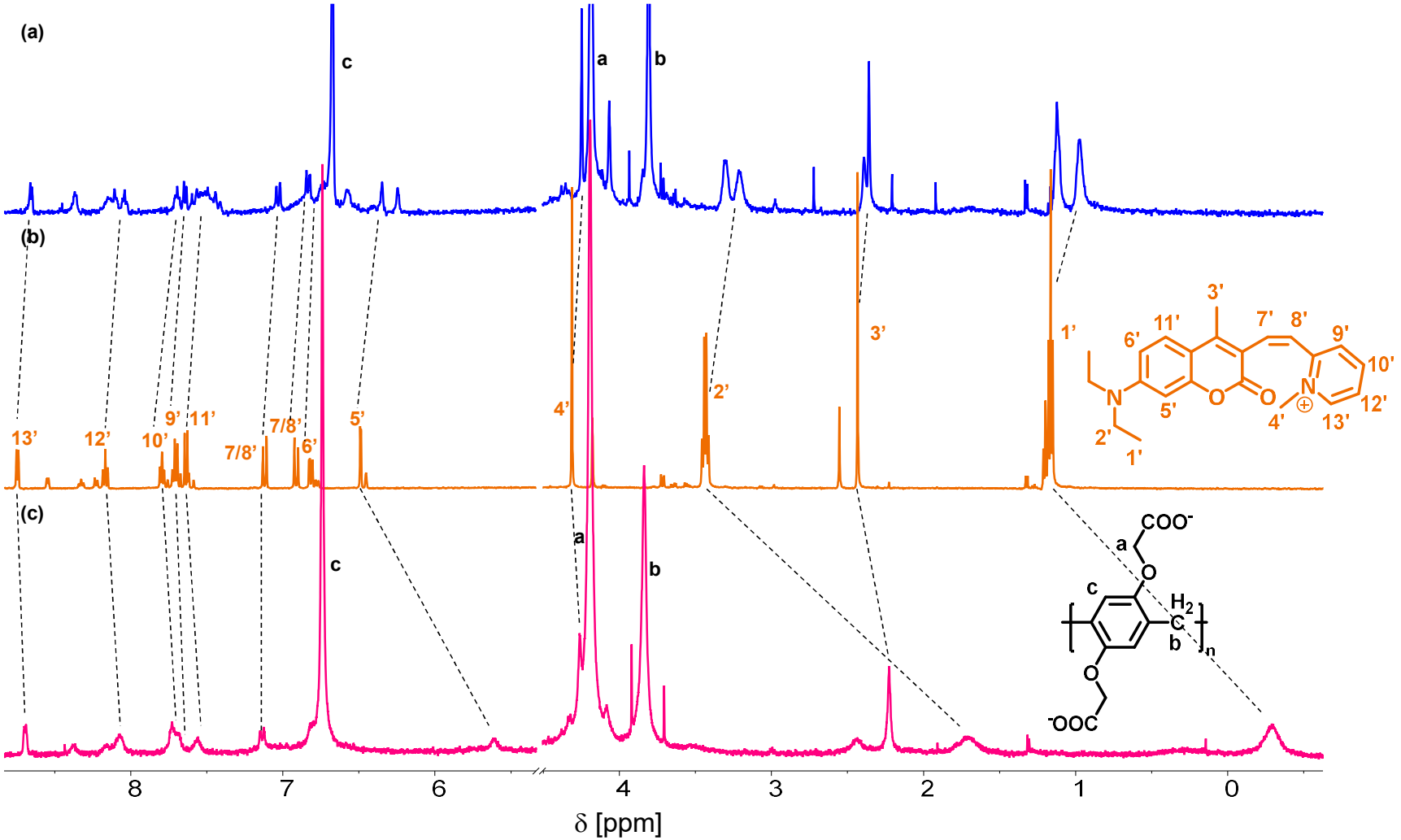


Fig. S4: (a) *trans*-CP + WP5 after 10 min irradiation with the green LED, (b) a *cis*-CP/*trans*-CP PSS mixture containing 75% *cis*-CP, (c) *trans*-CP + WP6 after 10 min irradiation with the green LED at 500 MHz, $D_2O$; [CP] = $6 \times 10^{-4}$ M.

## S5. Determination of the stoichiometry of the *trans*-CP-WPn complexes

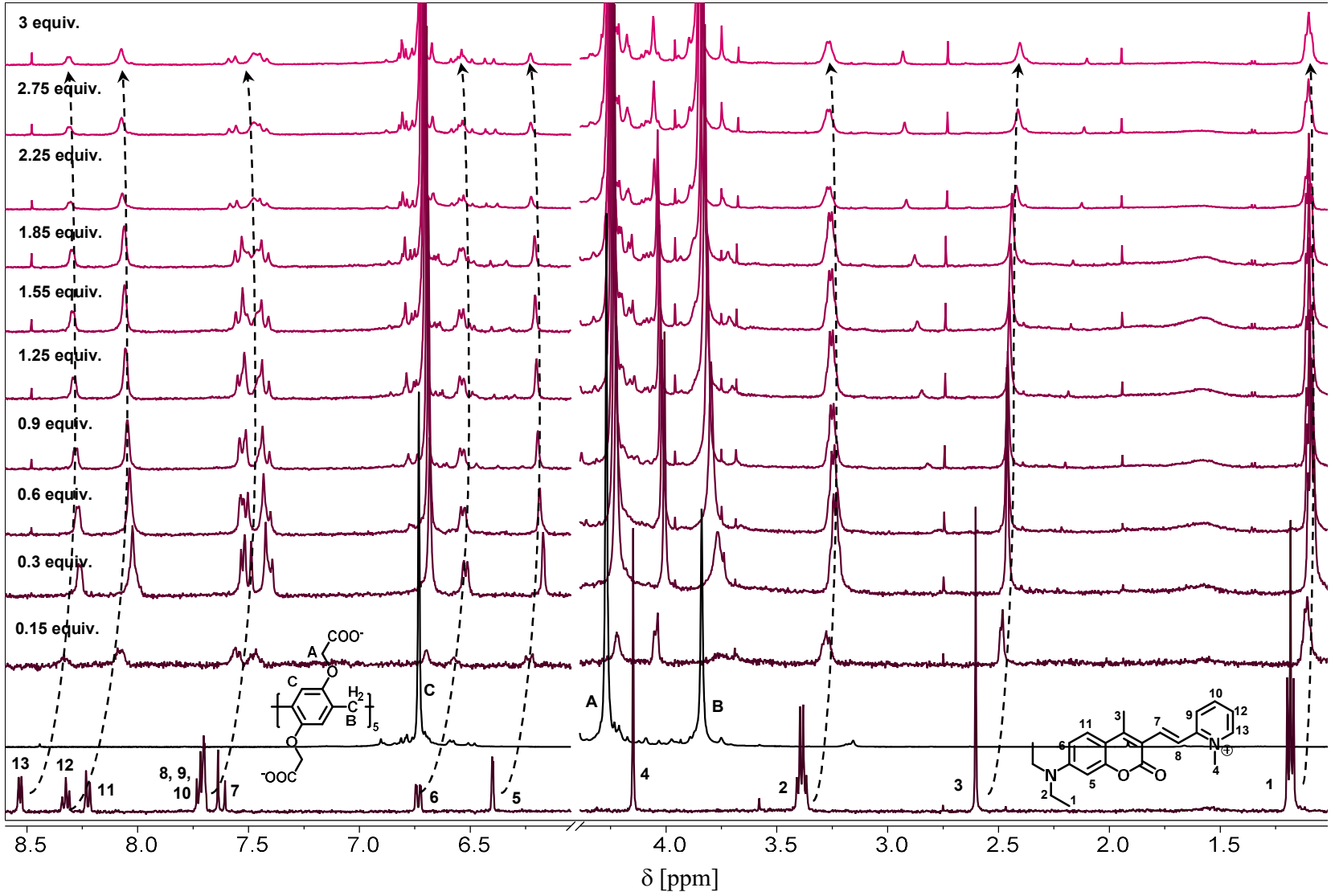


Fig. S5: $^{1}$H-NMR titration of *trans*-CP in $D_2O$ containing 0 – 3 equiv. of WP5, [CP] = $8\times10^{-4}$ M

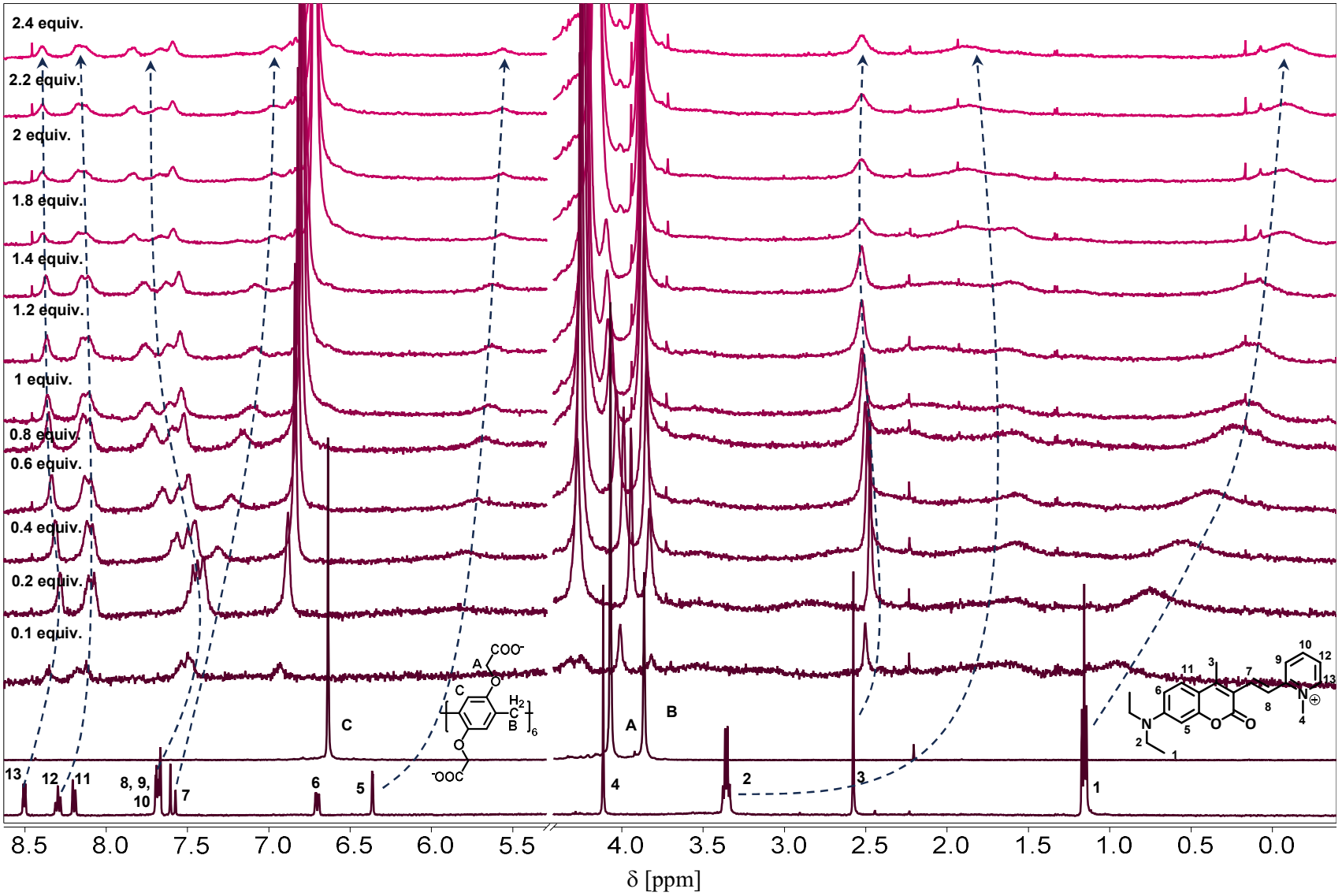


Fig. S6: $^{1}$H-NMR titration of *trans*-CP in $D_2O$ containing 0 – 2.4 equiv. of WP6, [CP] = $7\times10^{-4}$ M

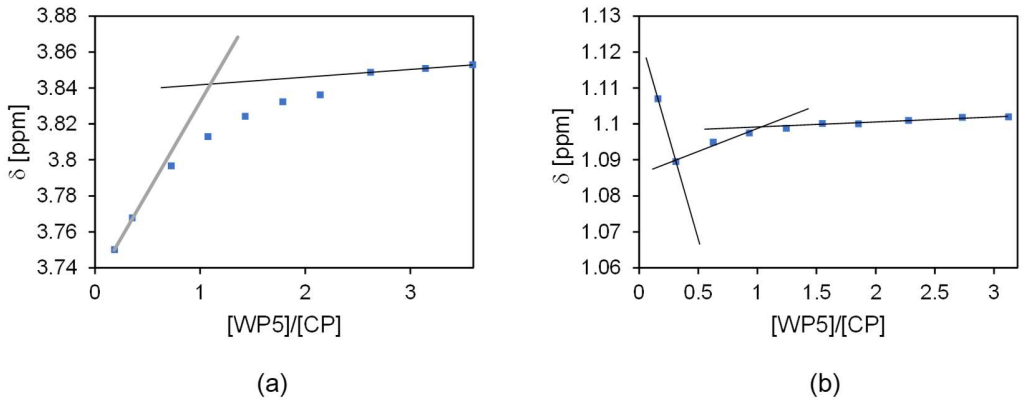


Fig. S7: Molar ratio plot for (a) **B** and (b) **1** protons in *trans*-CP·WP5-complex, [CP] = $8\times10^{-4}$ M

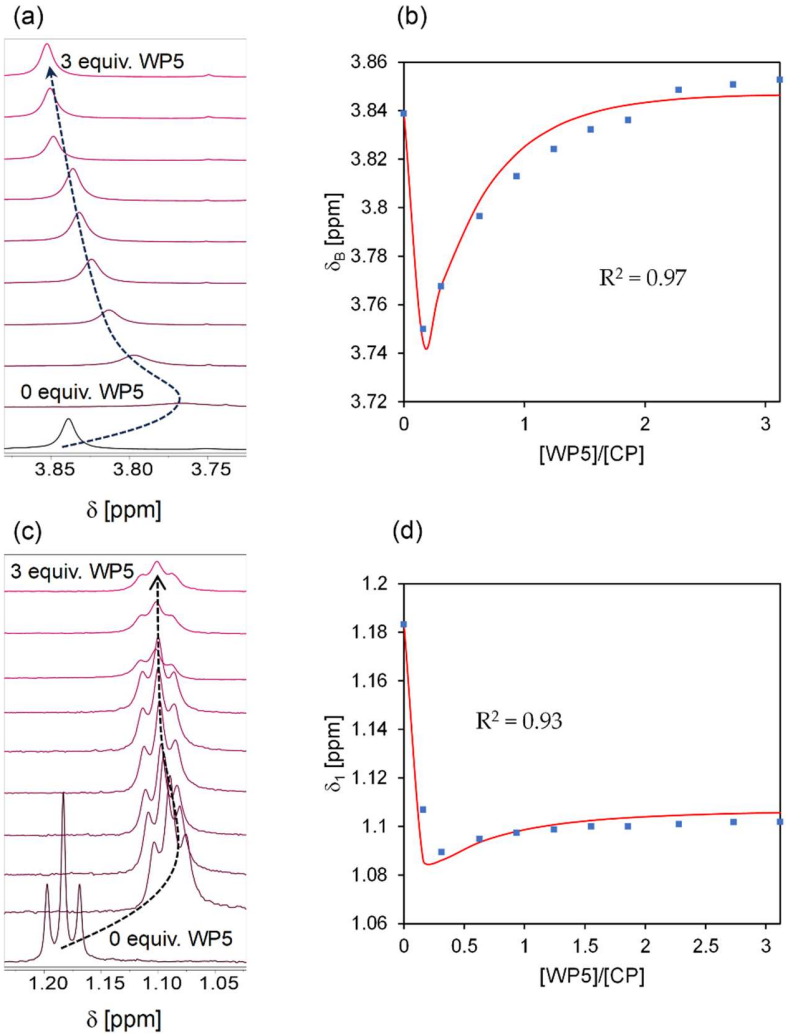


Fig. S8: Ranges of the $^{1}$H NMR spectra (500 MHz, $D_2O$) presenting protons **B** and **1** in *trans*-CP and 0 – 3 equiv. WP5 mixtures (a and c); binding constant least-squares fitting for **B** (b) and **1** (d) protons in *trans*-CP complex

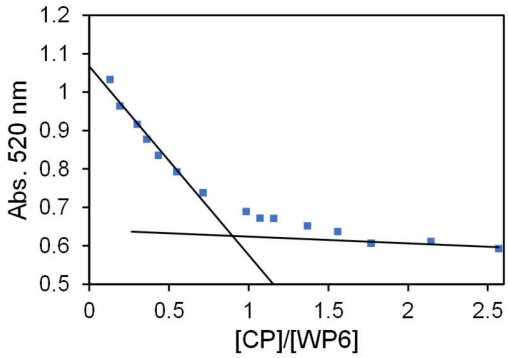


Fig. S9: Molar ratio plot for the *trans*-CP·WP6 complex, [CP] = $4\times10^{-5}$ M

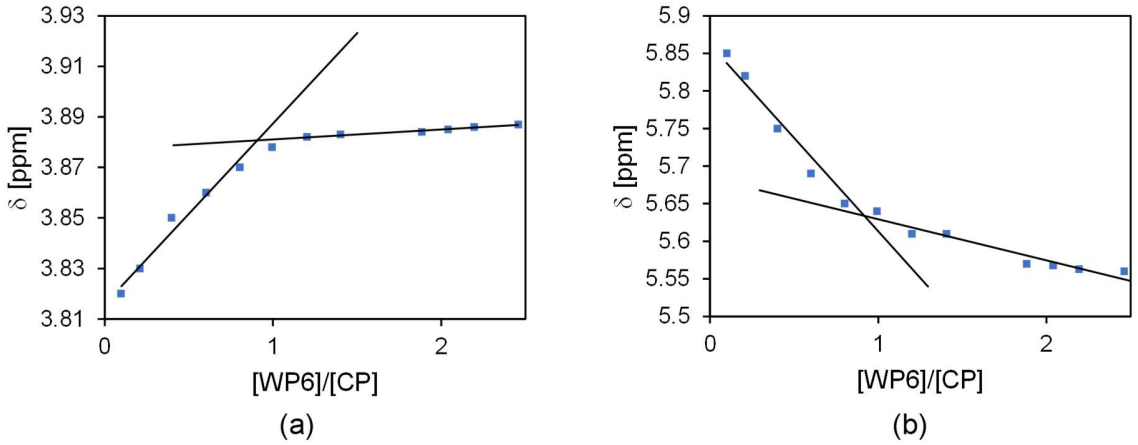


Fig. S10: Molar ratio plot for (a) **B** and (b) **5** protons in the *trans*-CP·WP6 complex, [CP] = $7\times10^{-4}$ M

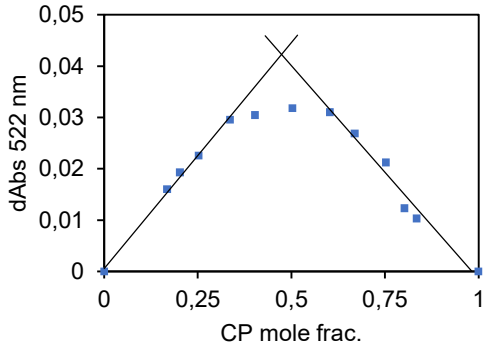


Fig. S11: Job's plot for determination of the stoichiometry of the *trans*-CP·WP6 complex; the sum of the concentrations of *trans*-CP and WP6 is $2\cdot10^{-5}$ M;

## S6. Theoretical calculations

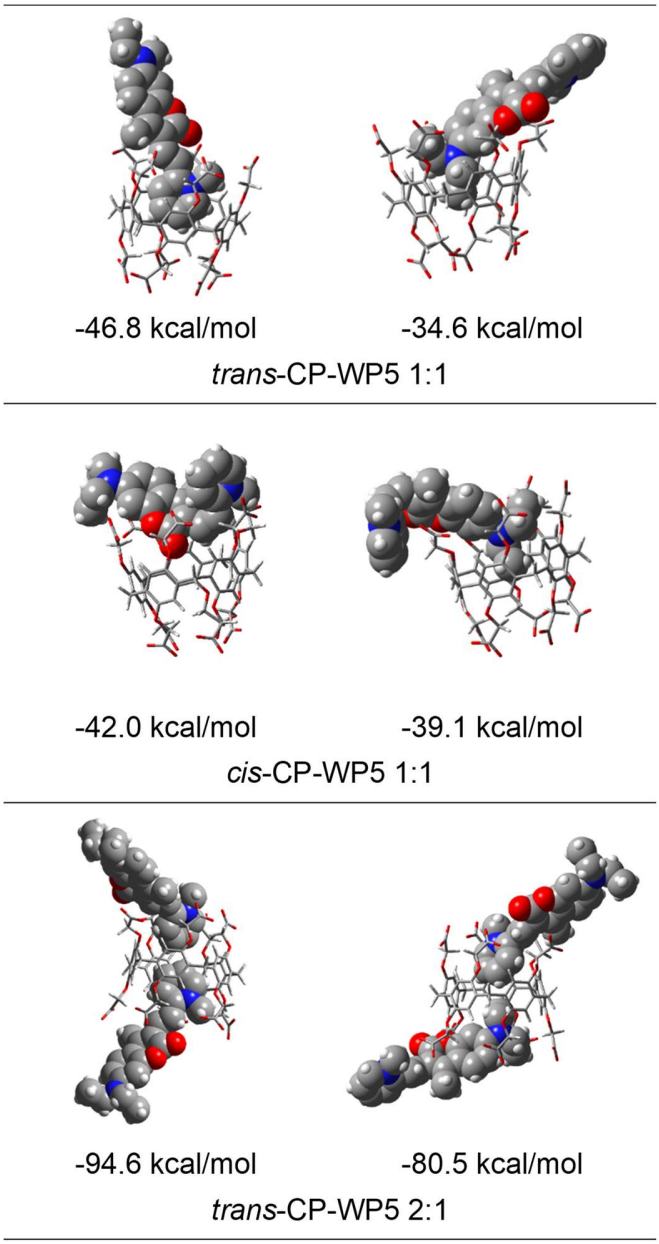


Fig. S12. Theoretically calculated structures and binding energies of CP-WP5 1:1 and 2:1 complexes