# ***Supplementary information***

# Supramolecular influence on cis-trans isomerization probed by ion mobility spectrometry

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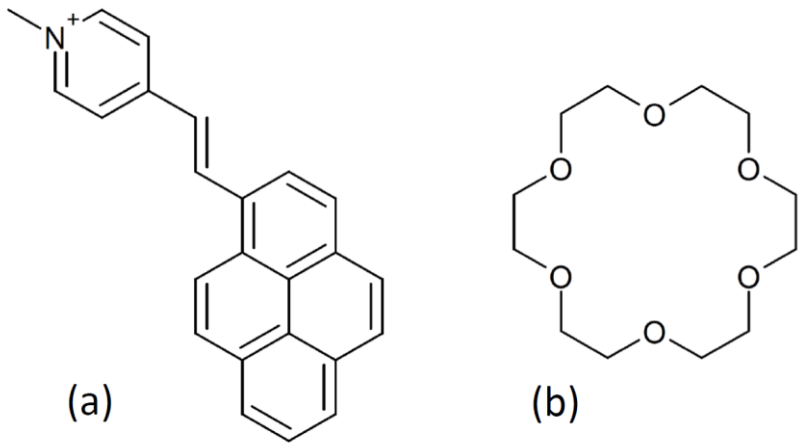


**Scheme S1**. Chemical structures for (a) 1-methyl-4-[2-(1-pyrenyl)vinyl]pyridinium (MPVP) and (b) 18-crown-6-ether (18C6).

**Table S1**: Characteristic angles $\theta_1$ and $\theta_2$ for the different rotamers of the lowest energy structures identified from the DFT/CC2 calculations.

| | MPVP | | | MPVP@18C6 | | |
|---|---|---|---|---|---|---|
| | ΔE (kJ/mol) | $\theta_1$ | $\theta_2$ | ΔE (kJ/mol) | $\theta_1$ | $\theta_2$ |
| *cis*-A | +9 | -27° | -52° | 0 | 57° | -90° |
| *cis*-B | +11 | 24° | -134° | +10 | -35° | -52° |
| *trans*-A | 0 | -7° | 166° | +19 | 5° | -160° |
| *trans*-B | +6 | -11° | -27° | +24 | -16° | -33° |

**Table S2**: Calculated excited states of *trans*-MPVP and *trans*-MPVP@18C6. $TE_V$ are the vertical transition energies and $TE_{0\text{-}0}$ the 0-0 transition energies. The level of theory is given in parenthesis. In the last column, $cTE = TE_V(CC2) + [\,TE_{0-0}(TDDFT) - TE_V(TDDFT)]$ is computed to estimate vibronic shifts for the comparison with experiment (see text for details). All energies are in eV.

| | $TE_V$ (TDDFT) | $TE_{0\text{-}0}$ (TDDFT) | $TE_V$ (CC2) | cTE |
|---|---|---|---|---|
| *trans*-MPVP-A | 2.56 | 2.48 | 2.27 | 2.19 |
| *trans*-MPVP-B | 2.55 | 2.37 | 2.25 | 2.07 |
| *trans*-MPVP-A@18C6 | 2.92 | - | 2.78 | - |

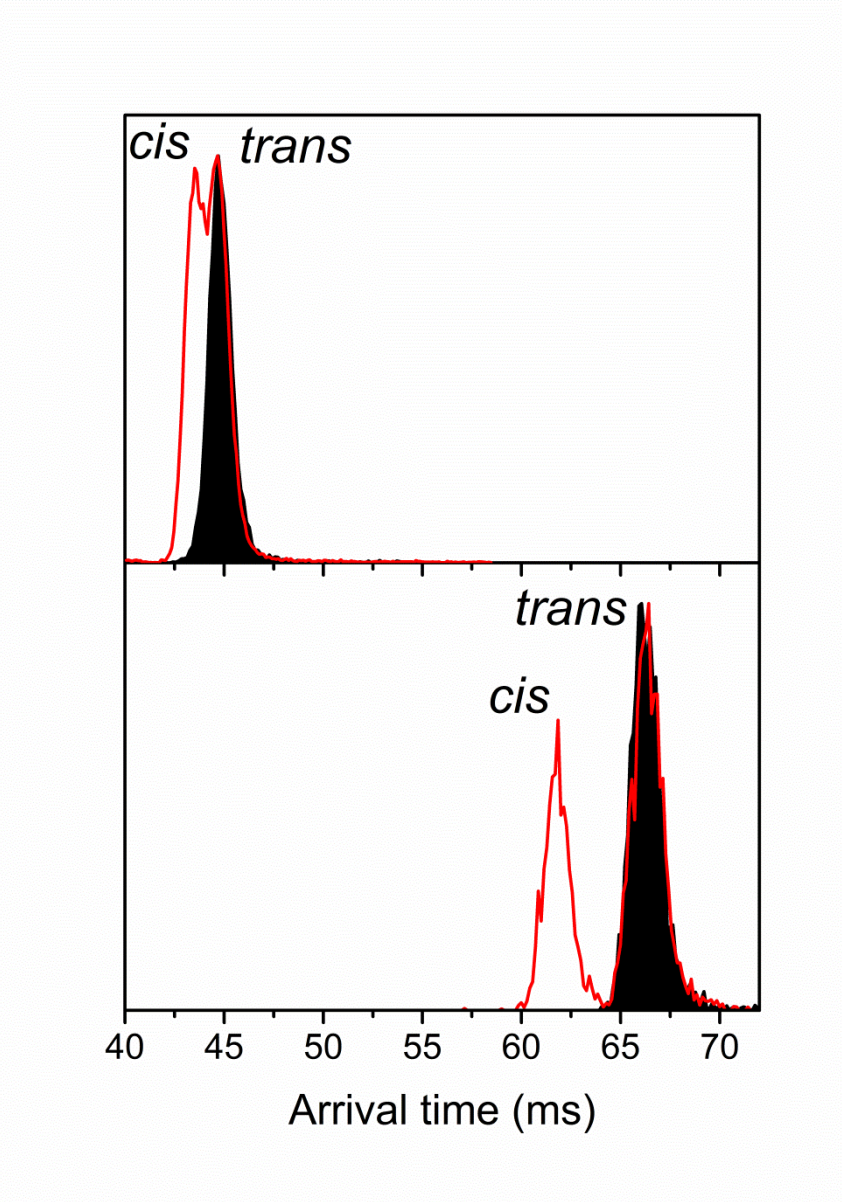


**Figure S1**. Arrival time distributions recorded for (a) MPVP and (b) MPVP@18C6 complex cations. Black shaded area: before sun light exposure, and red line: after sun light exposure of the solution. Drift conditions: He pressure 11.9 Torr, temperature 298 K, drift field 562.5 $V.m^{-1}$.

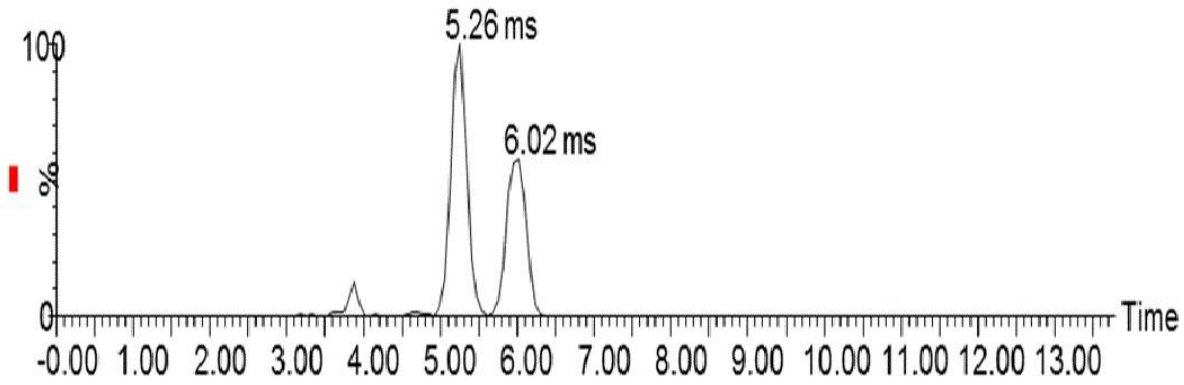


**Figure S2**. Arrival time distribution of *cis*-MPVP@18C6 (5.26 ms) and *trans*-MPVP@18C6 (6.02 ms) obtained with Synapt G2. Carrier gas was nitrogen. Pressure within the instrument was monitored using external gauge meters and it was at 1.7 Torr. The sampling and extraction cone potentials were 22 V and 3 V, respectively. The helium gas flow in the pre-(IM-MS) cell was 190 mL $min^{-1}$ with a wave velocity (WV) of 300 m $s^{-1}$ and a wave height (WH) of 50 V.

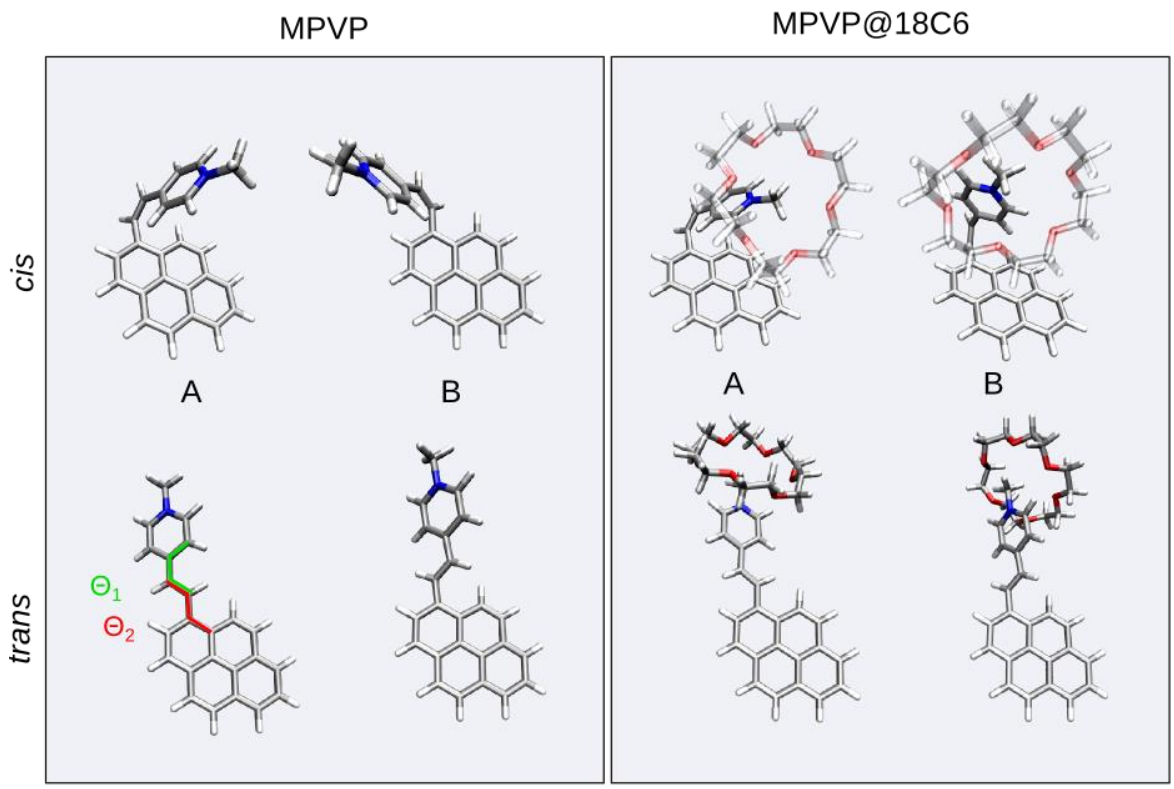


**Figure S3**: Optimized structures for the *cis* and *trans* forms of MPVP and MPVP@18C6 in the two identified rotameric forms, A and B (see table S1 for details).

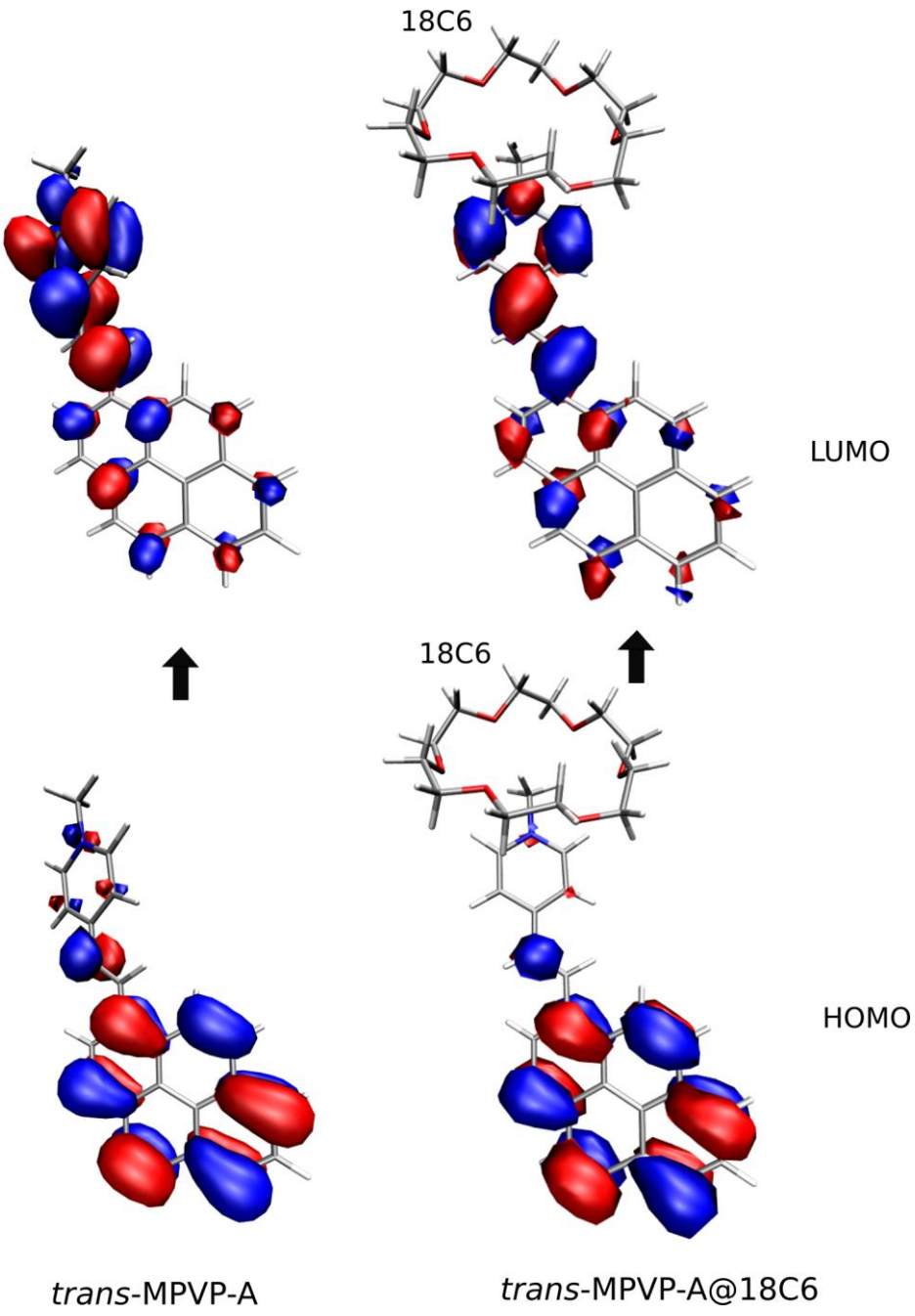


**Figure S4**: Leading orbital excitations in the first singlet transitions obtained at the CC2 level for *trans*-MPVP-A and its 18C6-complexed form.