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Electronic Supplementary Information

Cationic polythiophene-anionic fullerene pair in water and water-dioxane: studies on hydrogen bonding capabilities, kinetic and thermodynamic properties

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Qualitative approach to study solvation & co-solvation of ionic molecules

In the present work, the use of W-DI causes co-solvation to play a central role on the solution interactions under study. This is not a trivial phenomenon, especially when considering the ionic nature of the donor-acceptor pair, which jeopardizes the possibility to perform quantitative studies on solvation/co-solvation, which are out of the scope of the present work.

Previous studies on the solubility of bare (neutral, non-ionic) C_{60}, like those performed by Marcus et al.[1] or Cysewski[2] rely on datasets of physical and chemical solubility properties (e.g. the Kamlet-Taft hydrogen bond donicity), estimated (empirically or computationally) from a large variety of solvents. These datasets are then analysed using methods such as multivariate stepwise linear regression or a consonance solvents approach, in order to describe mechanistically (and predict) the solubility of C_{60}. To our knowledge, there are not datasets like these focused on water-soluble fullerenes, cationic polythiophenes (CPTs), or any other conjugated polyelectrolyte (CPEs).

Another quantitative approach is the use of the Hansen solubility parameters, which split interfacial energies into dispersive, polar, and H-bonding components. This approach also been used to analyze solubility/miscibility of bare C_{60}, using data from a broad selection of solvents and *non-conjugated* polymers, in the context of donor-acceptor pairs in organic photovoltaics.[3] However, there are not datasets like these focused neither in neutral (hydrophobic) conjugated polymers (CPs), nor in water-soluble fullerenes, CPTs or CPEs in general. The review by Yao and Tam[4] shows how only qualitative solvation analyses have been used in studies involving stimuli-responsive water-soluble (C_{60})polymers.

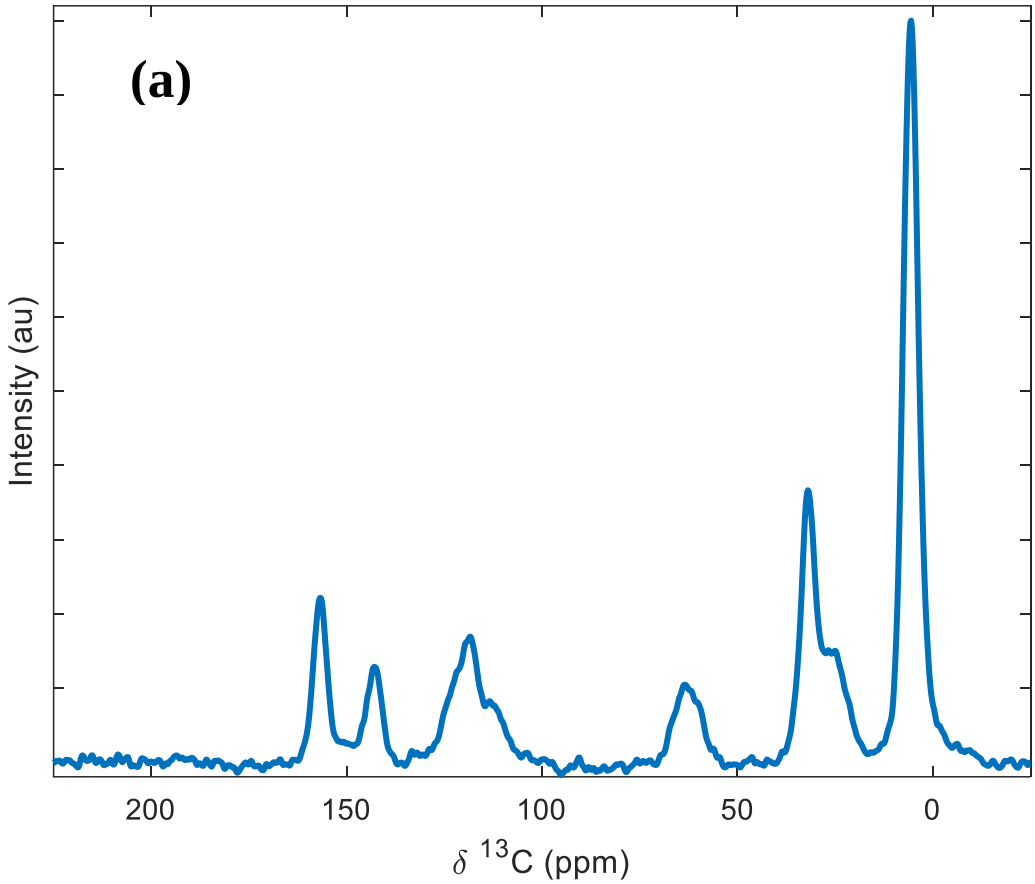
Besides this lack of empirical datasets from hydrophilic fullerenes and polymers, the use of binary solvent mixtures further compromise the possibility of performing quantitative studies on solvation. As stated in the review by Homocianu and Airinei,[5] the photophysical properties of solutes when dissolved in mixed solvents are influenced by the composition of systems (e.g. repartitioning of the cosolvent between solvation shell and bulk phase) and also by the intermolecular interactions that can be present (e.g. H-bonding, charge transfer, molecular associations, dipole–dipole and dipole–induced dipole

interactions). As a consequence, the physicochemical properties of many solvatochromic probes in binary solvents often show large deviations from the ideal behavior, as shown by the small correlation coefficients of microenvironment polarity (evaluated by Lippert–Mataga, Bakhshiev and Kawski–Chamma–Viallet polarity functions) observed for some fluorinated poly(oxadiazole-ether)s.[5]

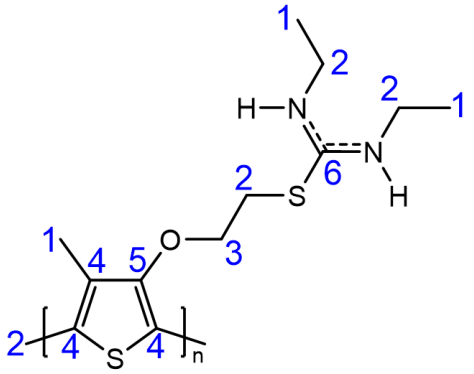
This lack of correlation of the Lippert-Mataga function has also been reported for CPEs in binary solvent systems, as reviewed by Burrows et al.,[6] on a study using DI as a cosolvent to break up clusters of an anionic CPE,[7] in which it was not possible to correlate spectral shifts with dielectric constant, either directly or with the Onsager or Lippert-Mataga functions. The data showed a poor correlation with the microscopic solvation parameter, however, a trend was observed in emission maxima with the parameter, suggesting that there is some specific interaction between the cosolvent and the polymer chromophoric component (i.e. the CPE backbone). MD simulations confirmed this assumption, showing preferential solvation of the backbone by the DI cosolvent, a “coating” displacing water from the immediate environment of the molecule, while the ionic parts are preferentially solvated by water, reducing interchain and side-chains interactions, in comparison with the system in water.[6]

The review by Marcus on the co-solvation of drugs in binary solvent mixtures,[8] is a perfect example on why a quantitative approach on co-solvation is beyond the scope of the present work, and the whole field of CPEs, to this date.

Carbon-13 Cross Polarization/Magic Angle Spinning Nuclear Magnetic Resonance (CP/MAS 13C-NMR)



(b)



δ^{13}C (ppm)	Assignment
5	1
32	2
64	3
119	4
143	5
157	6

Figure S-1. (a) ^{13}C CPMAS NMR spectrum of PT1; (b) Assigned structure and predicted ^{13}C Chemical Shift.

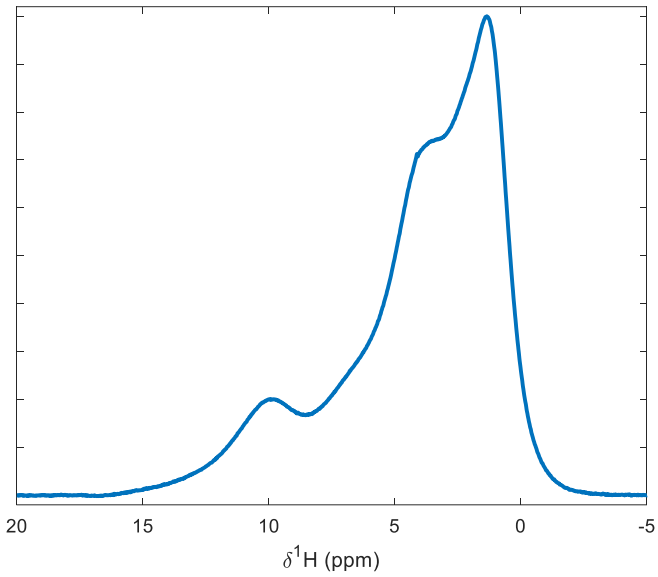


Figure S-2. ^{1}H MAS NMR spectrum of PT1.

Spectroscopic data

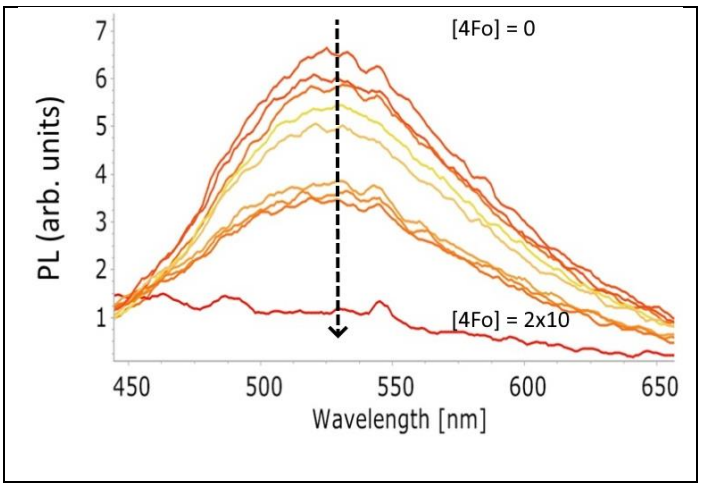


Figure S-3. Changes in the PL spectra of PT1 in W-DI due to increasing concentrations of 4Fo.

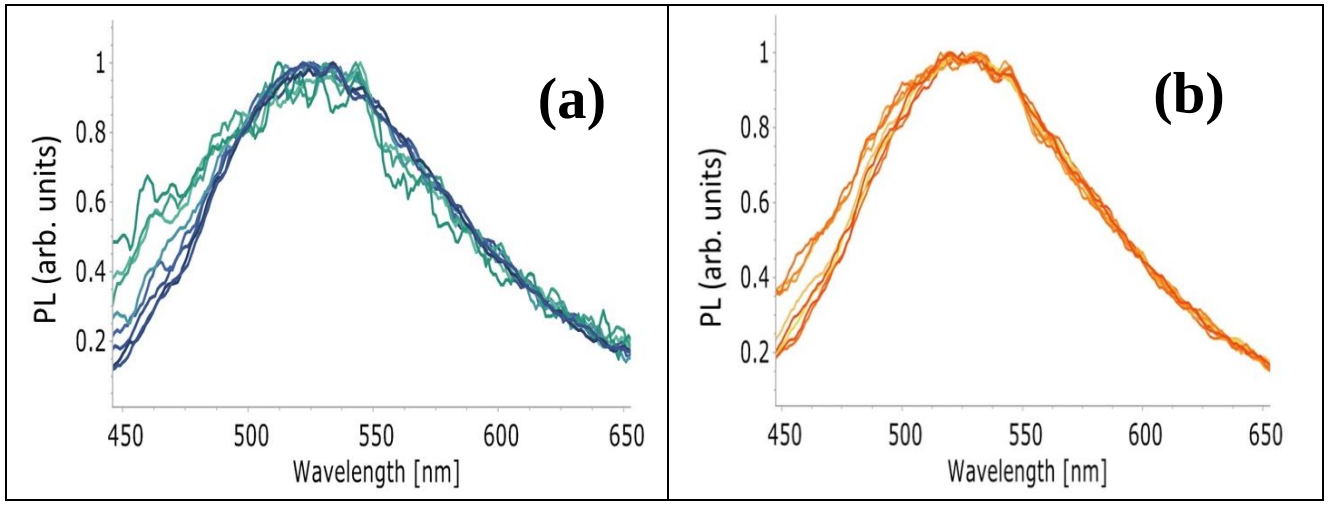


Figure S-4. Normalized PL spectra of PT1. Intensity decreases due to increasing amounts of 4Fo in (a) water and (b) W-DI.

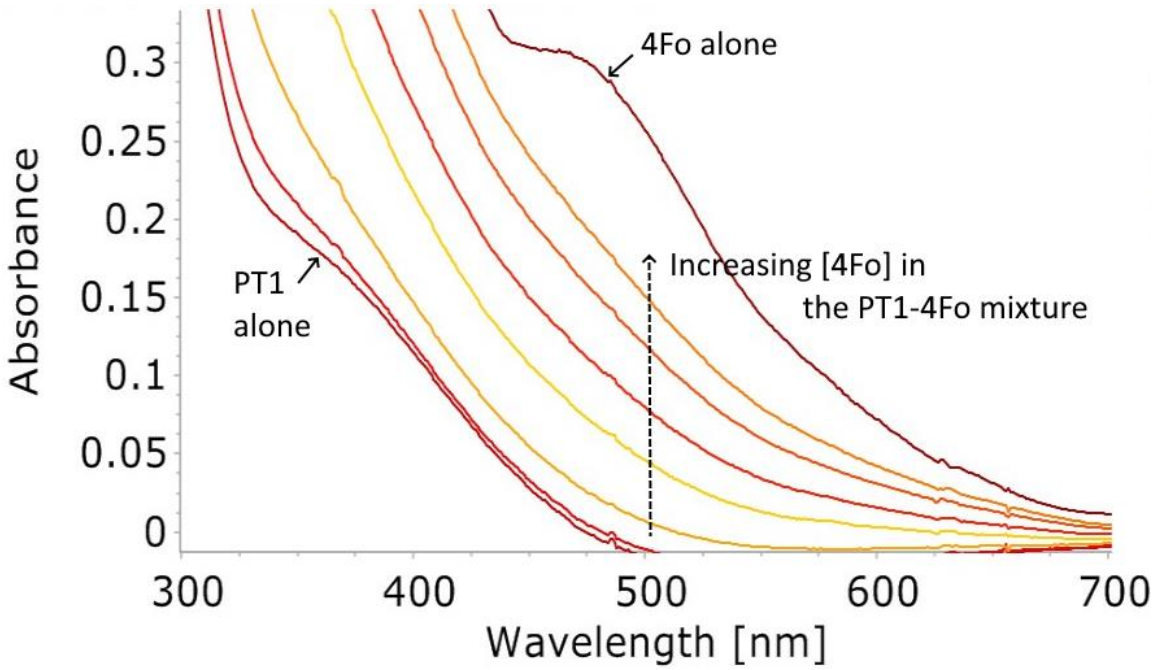


Figure S-5. Absorption spectra of PT1, 4Fo and the intermediate spectra of their mixtures, in W-DI.

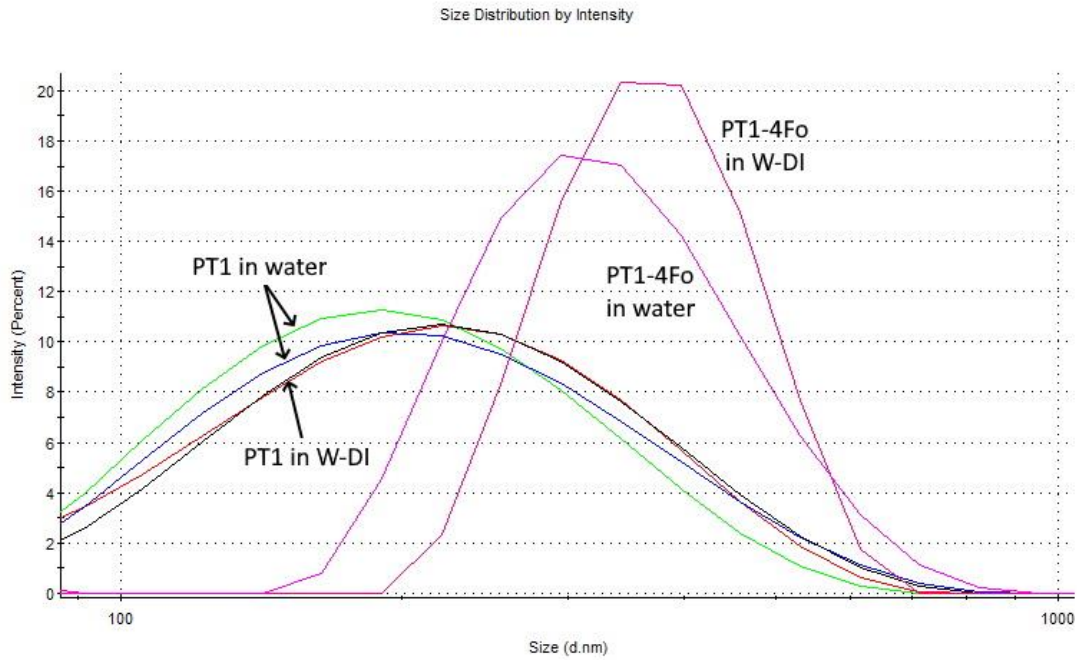


Figure S-6. DLS traces of PT1 solutions (0.105 mM) in water and W-DI in the absence or presence of 4Fo ($1.5x10^{-5}$ M).

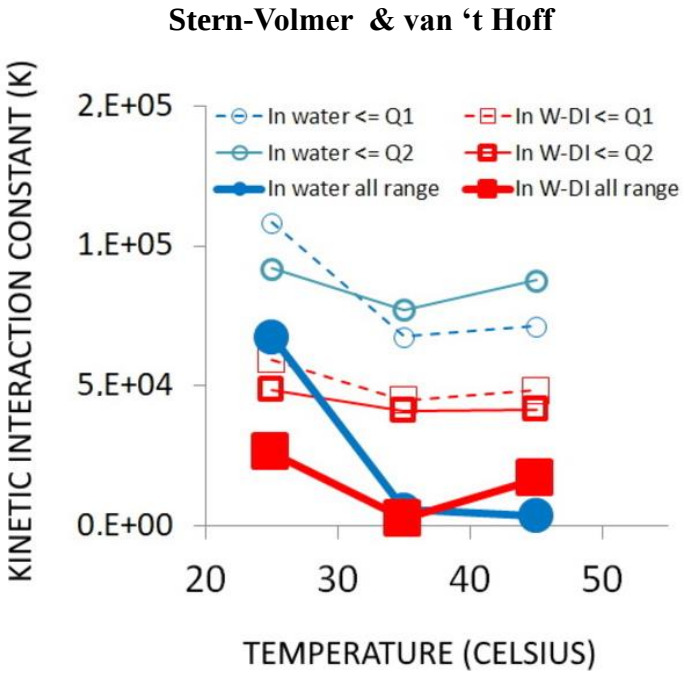


Figure S-7. Kinetic interaction constants obtained from equations 1 to 3 as indicated, at 25, 35 and 45 °C.

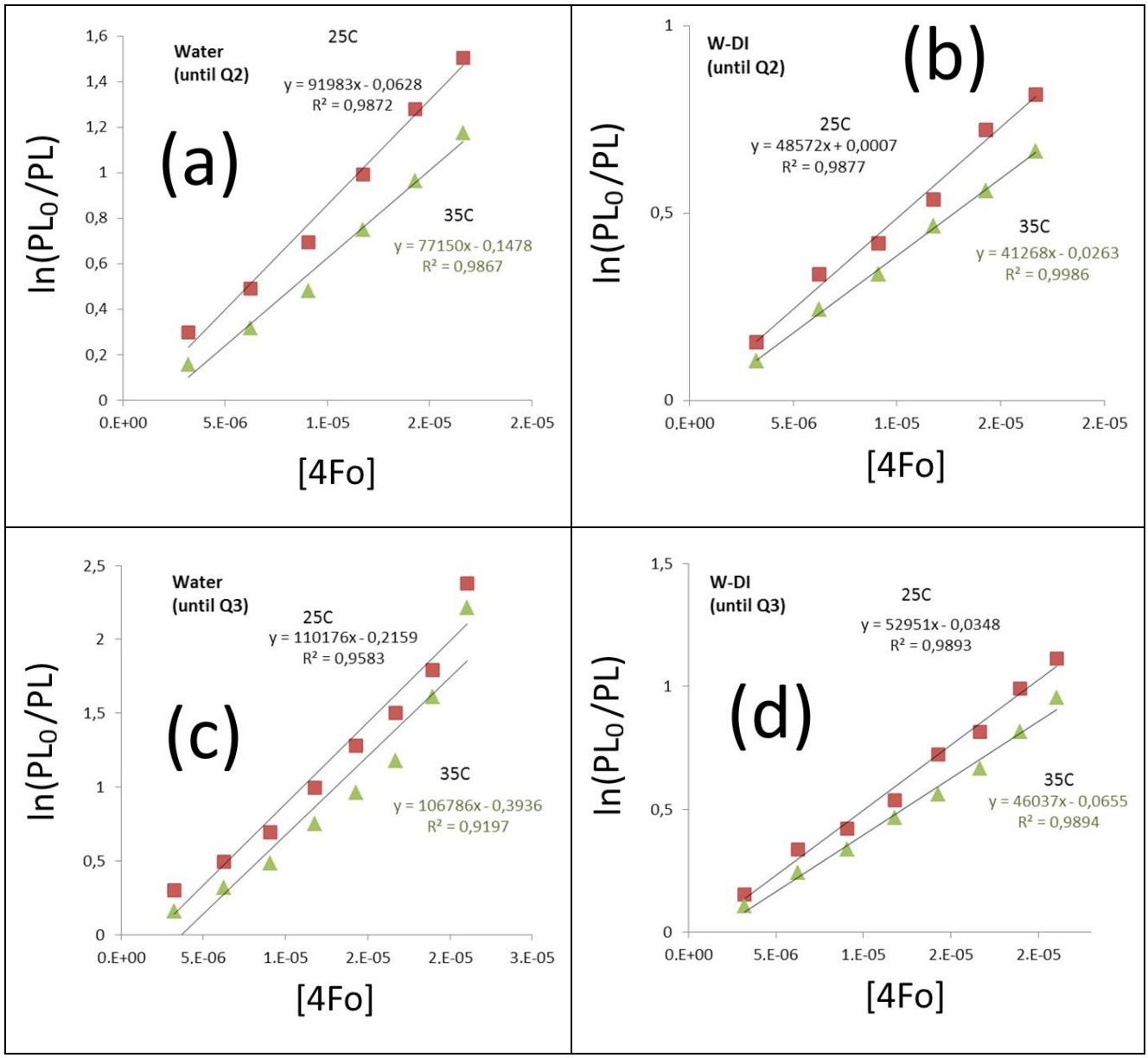


Figure S-8. Fittings to Perrin's model until Q2 in (a) water and (b) W-DI, together with fittings until Q3 in (c) water and (d) W-DI, at 25 and 35 °C.

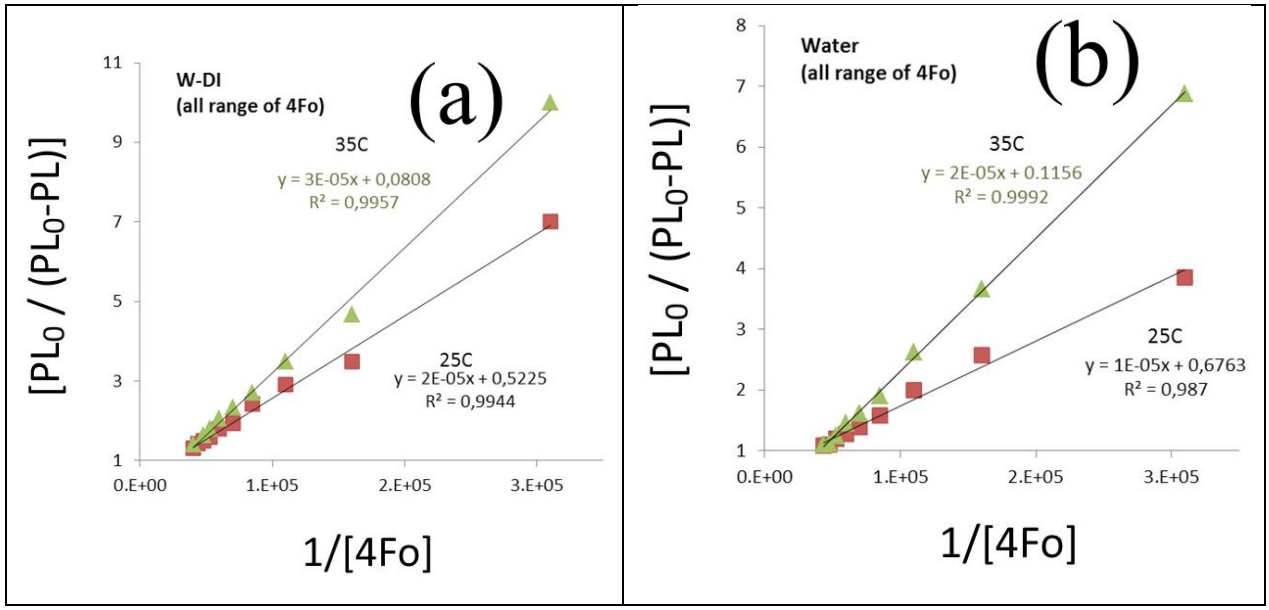


Figure S-9. Fittings using the general static quenching (GSQ) model using the data obtained in (a) water or (b) W-DI at 25 and 35 °C.

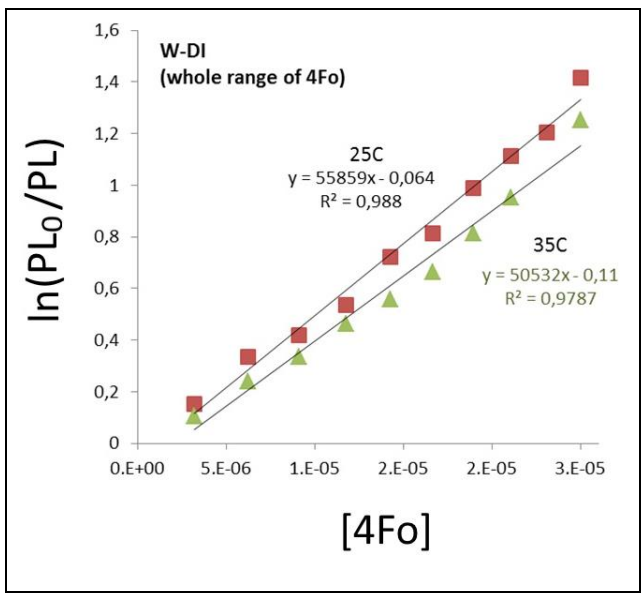


Figure S-10. Fittings to Perrin's model in the whole range of Q3 in W-DI, at 25 and 35 °C.

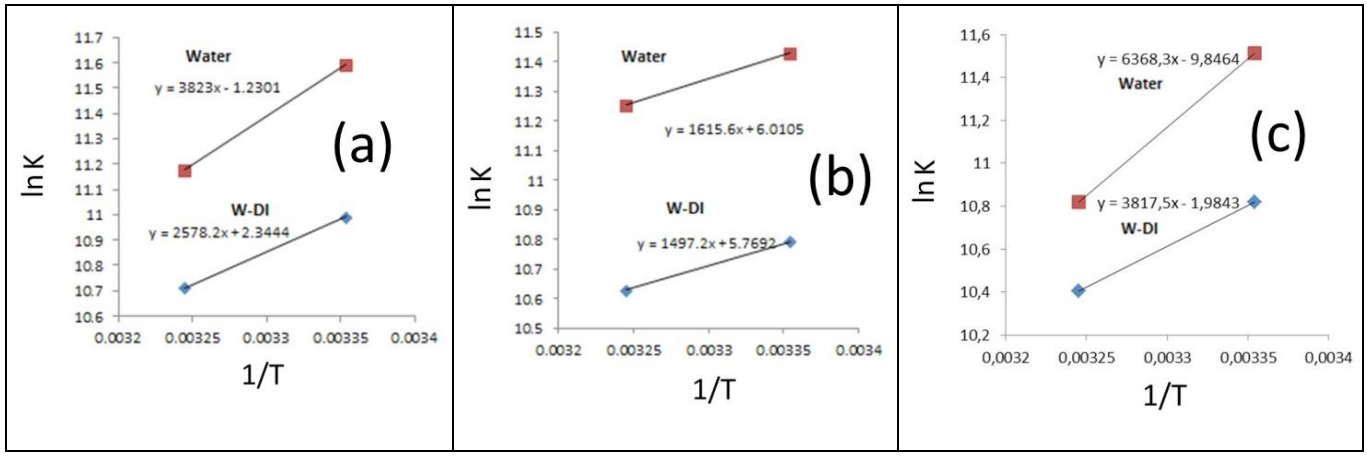


Figure S-11. van 't Hoff plots built using kinetic interaction constants obtained in water and W-DI, using (a) regular SV model with data of [4Fo] until Q1, (b) Perrin's model with data of [4Fo] until Q2 and (c) GSQ model with data from the whole range of [4Fo].

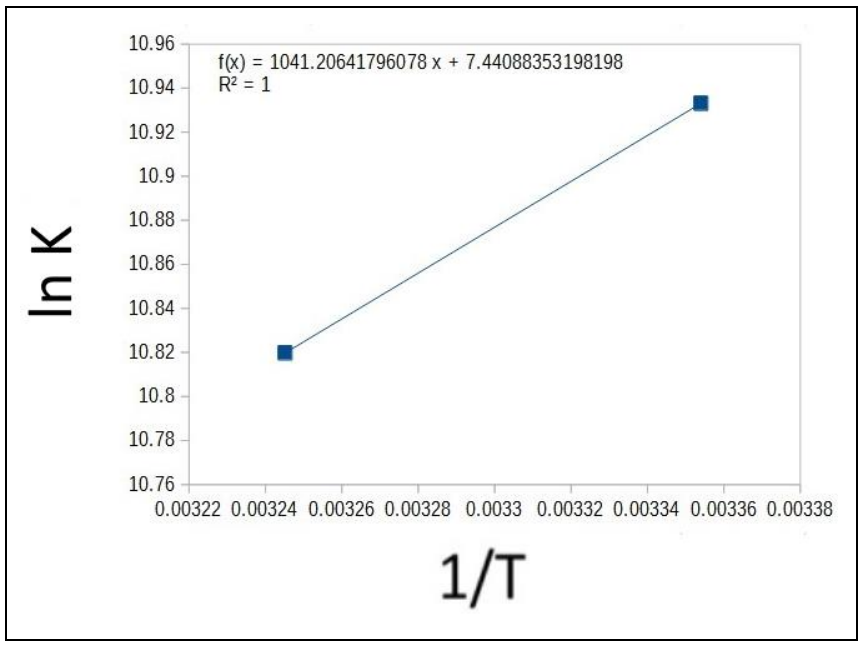


Figure S-12. van 't Hoff plot built using kinetic interaction constants from the Perrin model from the whole range of [4Fo] in W-DI.

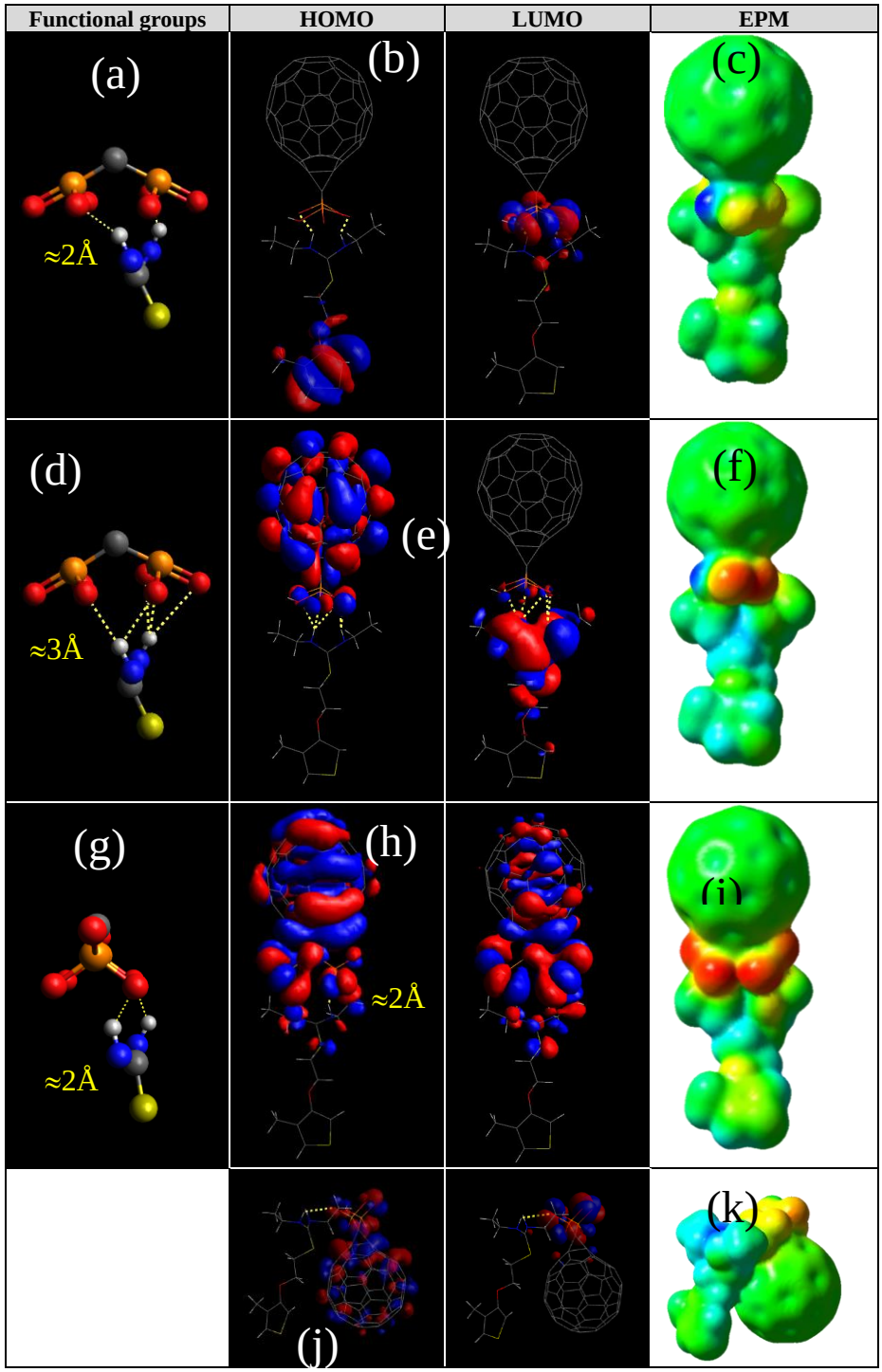


Figure S-13. Results of single-point calculations at the B3LYP/3-21G(*) level of theory in vacuum, on arbitrary spatial arrangements between isothiouronium (T1) and bisphosphonate (2Fo): (a,d,g) zoom to the isothiouronium and biphosphonate groups in each arbitrary complex; (b,e,h,j) electronic density distributions at the HOMO and LUMO of the T1-2Fo pair; (c,f,i,k) electrostatic potential maps (EPMs) of each arbitrary complex. H-bonds are shown as yellow dashed lines.

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