Supporting Information

Computational Analysis

The energy of interaction between a complexing agent and 3NP was determined as the difference between the reported energy of each molecule placed in proximity to each other (interacting) and separately (non-interacting). Molecules that yielded a significant (<-5 kcal/mole) prediction of beneficial interaction during the formation of the complex were deemed appropriate for experimental verification. The calculated energies are listed below in table 1.

Table 1. Calculated computational energies of interaction between selected complexing agents and 3NP. All values are reported in kcal/mol.

Complexing Agent	$E_{separate}$	$E_{interacting}$	ΔE
β-Alanine[z]	-115.5	-140.9	-25.4
Guanidineacetic Acid[z]	-200.1	-224.8	-24.6
γ-Aminobutyric Acid[z]	-94.2	-117.7	-23.5
Taurine[z]	29.33	6.8	-22.5
3-Aminobenzoic acid	-16.6	-44.9	-15.7
Succinamic Acid	-72.0	-86.0	-14.0

Individual X-Ray Diffraction

The XPRD images shown in overlap during the body of the communication are shown separately for detail in this section. It must be noted that the count intensity for the3ABA sample XRD has lower values than those shown in Figure 4 of the paper because the whole XRD curve was shifted upward for clarity purposes of that image, the relative intensity and position of the peaks was not modified.

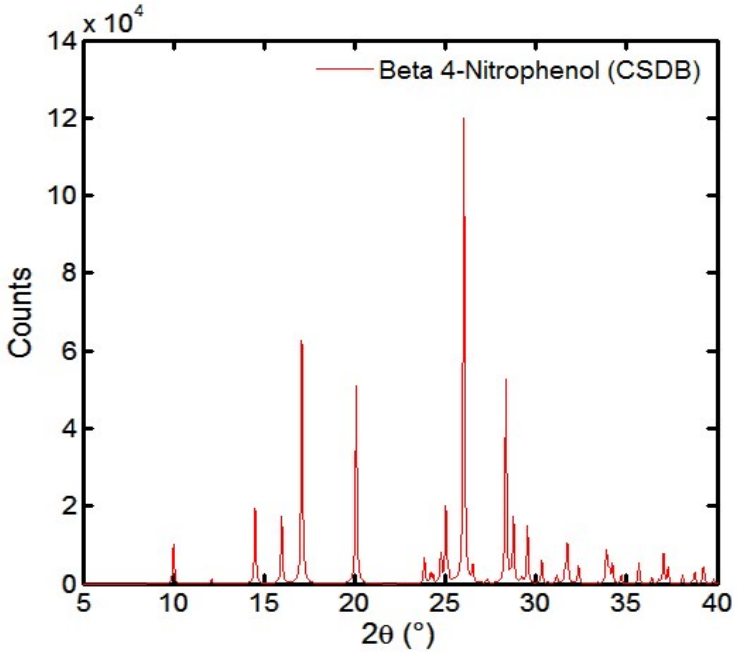

Fig 1. Theoretical XPRD for the beta polymorph of 4NP, obtained from the Cambridge Structural Database.

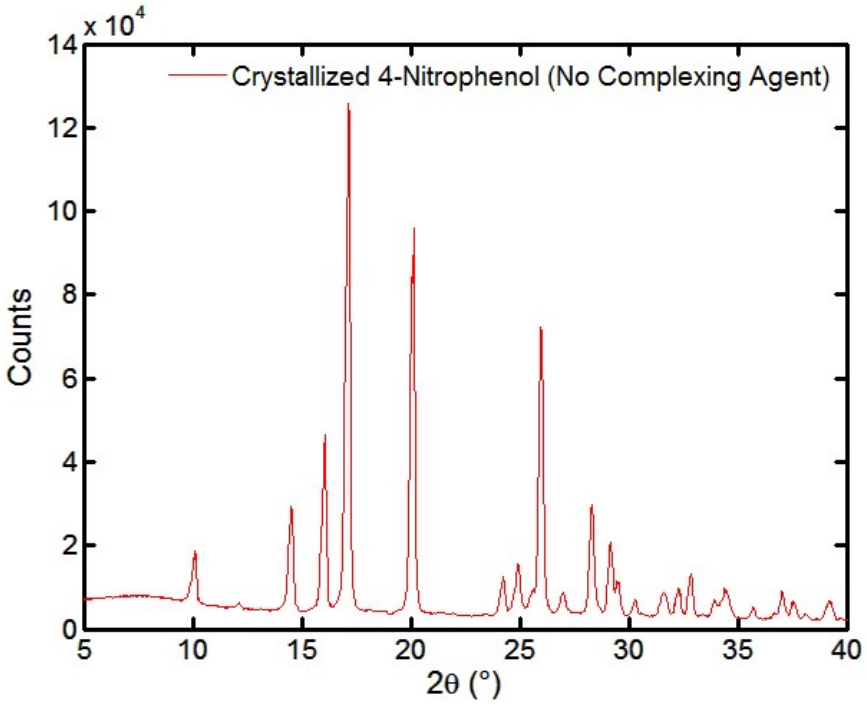

Fig 2. Experimentally obtained XPRD of 4NP, taken from a sample crystallized in water with no complexing agent. The graph matches with that of the beta form in Fig 1.

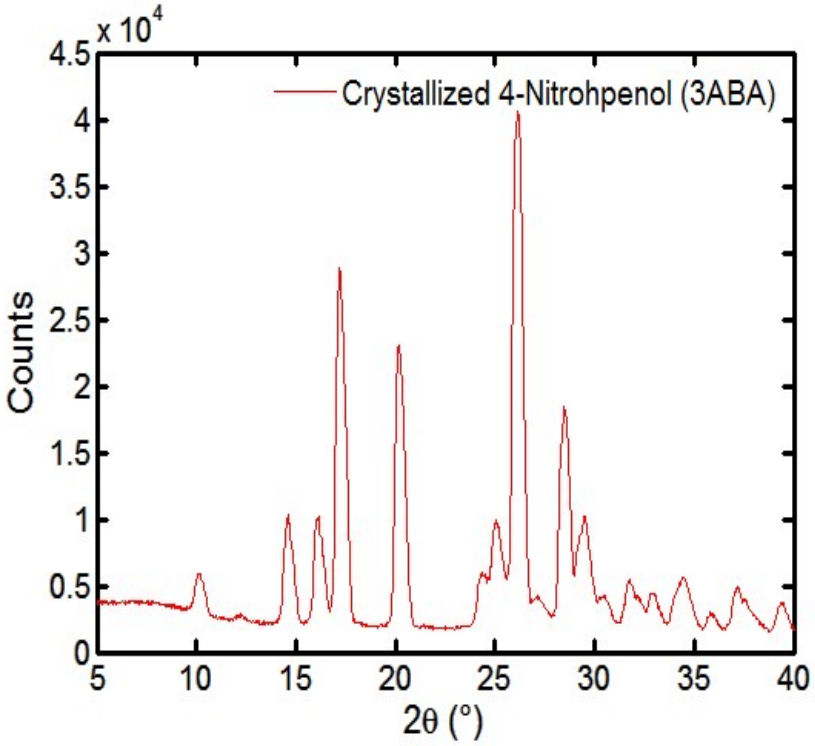

Fig 3. Experimentally obtained XPRD of 4NP, taken from a sample crystallized in water with 3ABA as the complexing agent. The graph matches with that of the beta form in Fig 1.

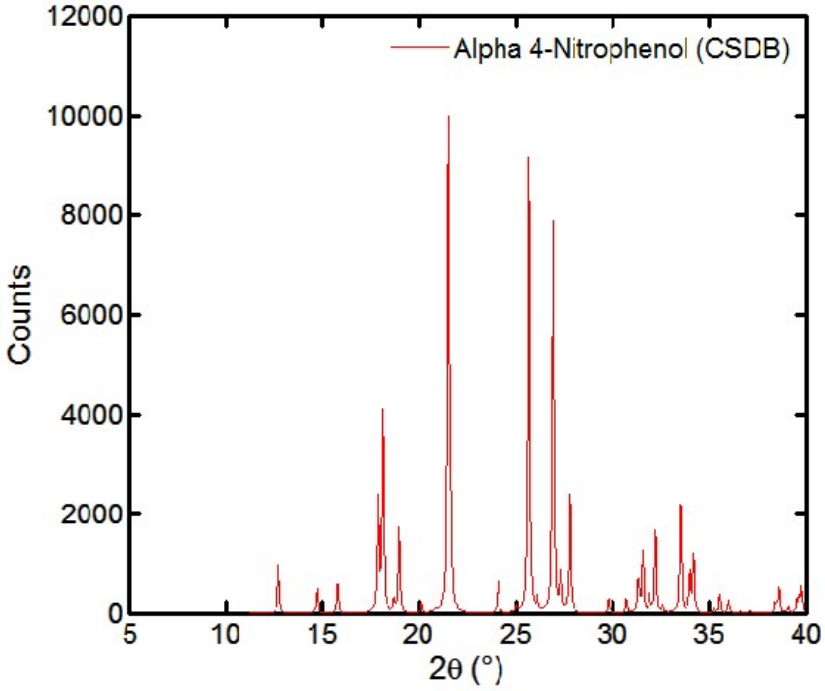

Fig 4. Theoretical XPRD for the alpha polymorph of 4NP, obtained from the Cambridge Structural Database.

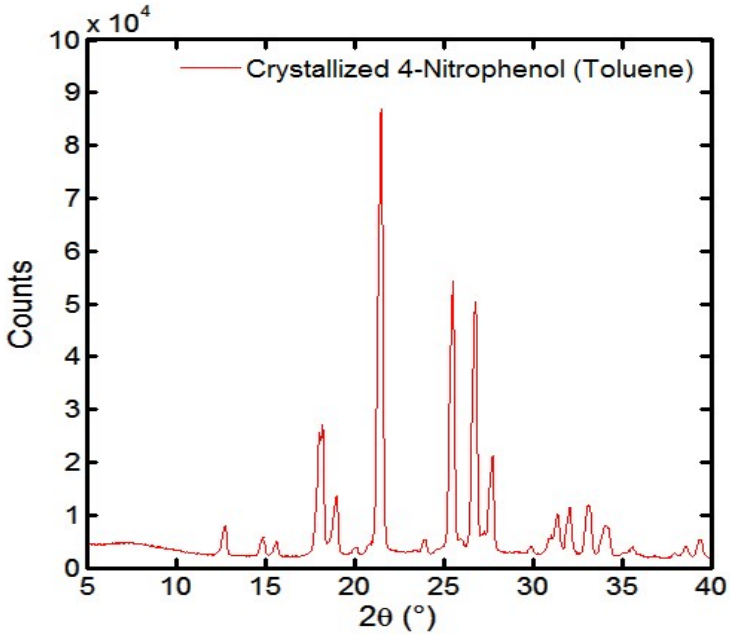

Fig 5. Experimentally obtained XPRD of 4NP, taken from a sample crystallized in toluene with no complexing agent. The graph matches with that of the alpha form in Fig 4.

Crystallization Data

The individual results for the crystallization experiments are shown below. The data shown corresponds to each of the batches performed in triplicate following the procedure outlined in the main manuscript.

Table 2. Experimental data for the purity of 4NP after crystallization in water. The results are presented in terms of percent weight of 3NP remaining in the solid product.

Experiment	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5	Exp. 6	Exp. 7	Exp. 8	Exp. 9	Exp. 10	Exp. 11	Exp. 12
Control	3.04	3.07	3.03	2.64	2.88	2.84	3.19	2.49	2.92	2.33	2.73	2.63

Experiment	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
Second Crystallization	0.21	0.19	0.17	N/A	N/A	N/A
β-Alanine	2.32	2.47	2.49	N/A	N/A	N/A
Guanidine Acetic Acid	1.40	1.47	1.44	2	N/A	N/A
γ-Aminobutyric Acid	1.18	2.19	2.13	N/A	N/A	N/A
Taurine	2.07	1.93	1.99	N/A	N/A	N/A
3-Aminobenzoic Acid	0.52	0.53	0.51	0.41	0.37	N/A
Succinamic Acid	1.46	0.86	1.33	1.35	0.4	1.05

Experiment	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
3ABA 3.9 mg/ml	1.93	2.03	2.07	N/A	N/A	N/A
3ABA 5.9 mg/ml	0.68	0.61	0.24	0.52	0.49	0.62
3ABA 7.9 mg/ml	0.52	0.53	0.51	0.41	0.37	N/A
3ABA 9.9 mg/ml	0.28	0.34	0.28	N/A	N/A	N/A

Table 3. Experimental data for the yield of 4NP after crystallization in water. The results are presented in terms of percent weight of 4NP recovered with respect to the original amount in the batch.

Experiment	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5	Exp. 6	Exp. 7	Exp. 8	Exp. 9	Exp. 10	Exp. 11	Exp. 12
Control	92.0	91.6	91.8	90.0	90.3	89.8	90.2	91.2	90.8	90.1	90.0	89.9

Experiment	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
Second Crystallization	82.6	82.1	82.3	N/A	N/A	N/A
β-Alanine	90.5	90.8	91.3	N/A	N/A	N/A
Guanidine Acetic Acid	91.4	90.9	90.4	91.4	N/A	N/A
γ-Aminobutyric Acid	91.4	91.4	89.4	N/A	N/A	N/A
Taurine	91.4	91.1	91.3	N/A	N/A	N/A
3-Aminobenzoic Acid	89.3	89.0	88.8	89.8	89.1	N/A
Succinamic Acid	91.5	91.5	91.0	90.0	90.1	89.7

Experiment	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
3ABA 3.9 mg/ml	90.1	90.1	89.9	N/A	N/A	N/A
3ABA 5.9 mg/ml	91.2	89.4	91.5	89.6	90.3	89.4
3ABA 7.9 mg/ml	89.3	89.0	88.8	89.8	89.1	N/A
3ABA 9.9 mg/ml	89.9	91.5	90.4	N/A	N/A	N/A

Membrane Experiments

The curves shown in figures 6 and 7 show the change in concentration over time of the retentate and permeate in the membrane experiments. The values reported in the manuscript are taken as the average of the rejection coefficient of the last three data points reported.

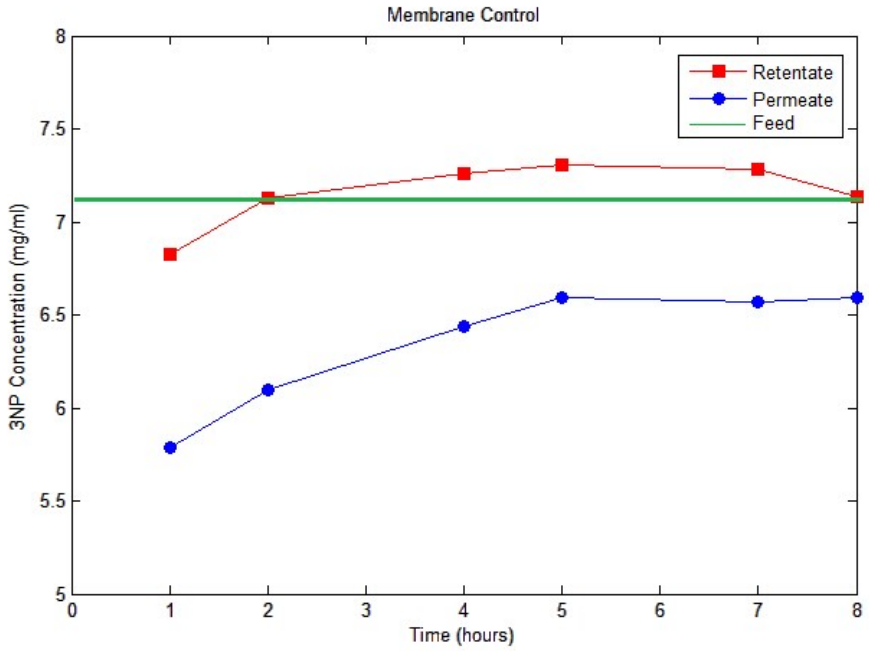

Fig 6. Evolution of the retentate and permeate concentrations over time in the control membrane experiment (no complexing agent used).

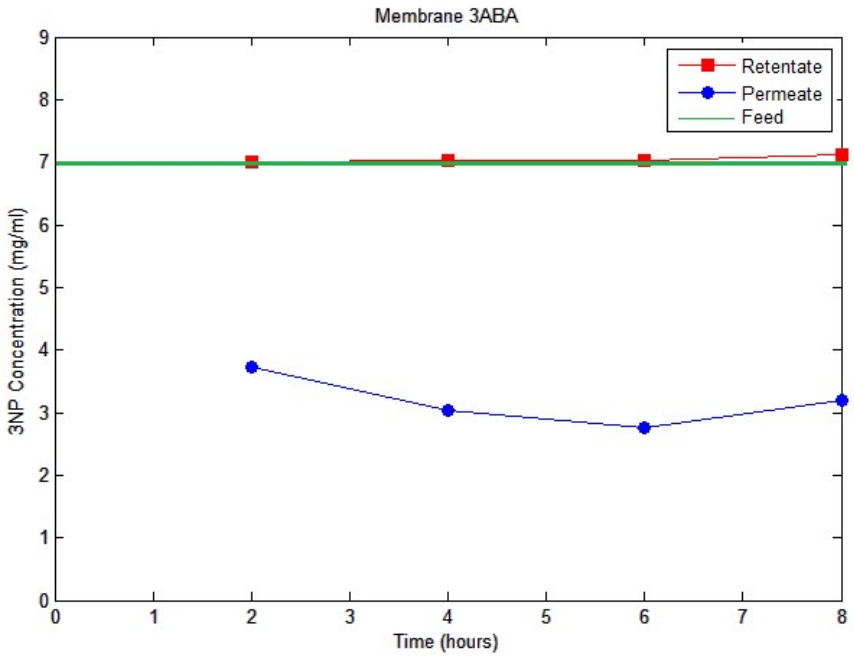

Fig 7. Evolution of the retentate and permeate concentrations over time in the 3ABA+3NP membrane experiment.

TGA testing of nitrophenols

TGA was used to optimize the drying conditions of the samples in the crystallization experiments. TGA was performed in order to compare the evaporation and sublimation profiles of the nitrophenols. This was done because it was observed that upon long exposure at medium temperatures (greater than 40 at °C) in a vacuum oven (25 inHg of vacuum) the composition of the crystallized solids would change, with a decrease in the relative amount of 3NP. The TGA curves are shown in figure 8.

The data in figure 8 shows that 3NP is more easily sublimated than 4NP. This result is expected given that 3NP has a lower boiling point than 4NP and it is expected to have a higher vapour pressure. This is evidenced by the fact that a substantially larger mass fraction of 3NP is lost upon reaching 100 °C. Subsequently, 3NP was completely removed at almost 25 °C lower temperature than 4NP. The heating profiles used for both compounds were identical and follow the program described in the experimental section. As a consequence of these results, the crystallization samples of the purification experiments were dried using a vacuum oven held at 25 °C for 12 hours. Under these conditions no changes in relative nitrophenol concentration were observed.

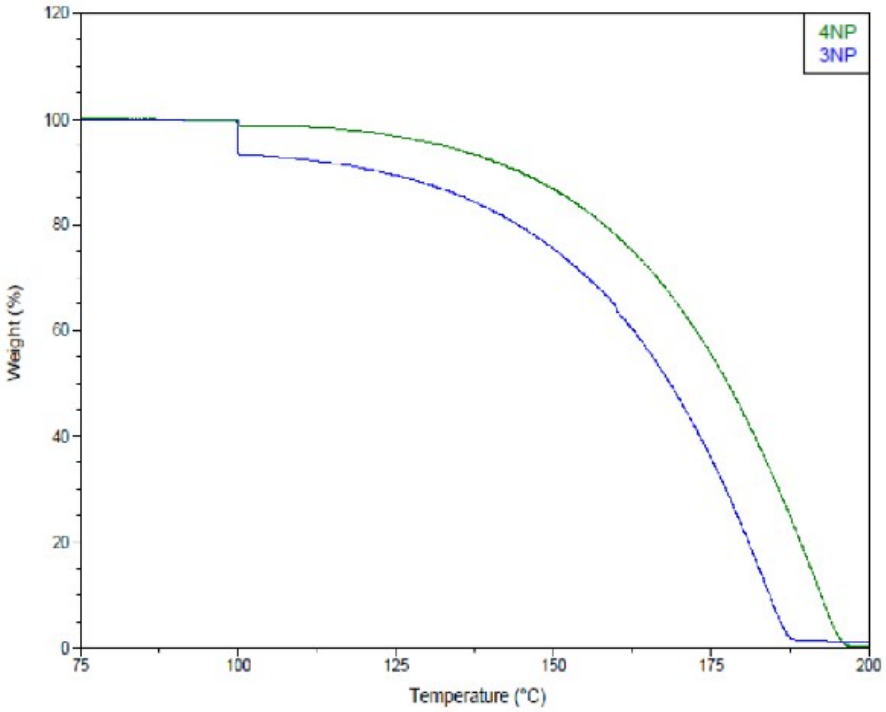

Fig 8. TGA curve of 3NP and 4NP. The curves are overlapped to show the differences in mass loss between the two compounds.