

Exploring Supramolecular Chemistry as an Innovative Strategy for Pyridine Guest Separations When Employing a TADDOL Derivative as the Host Compound

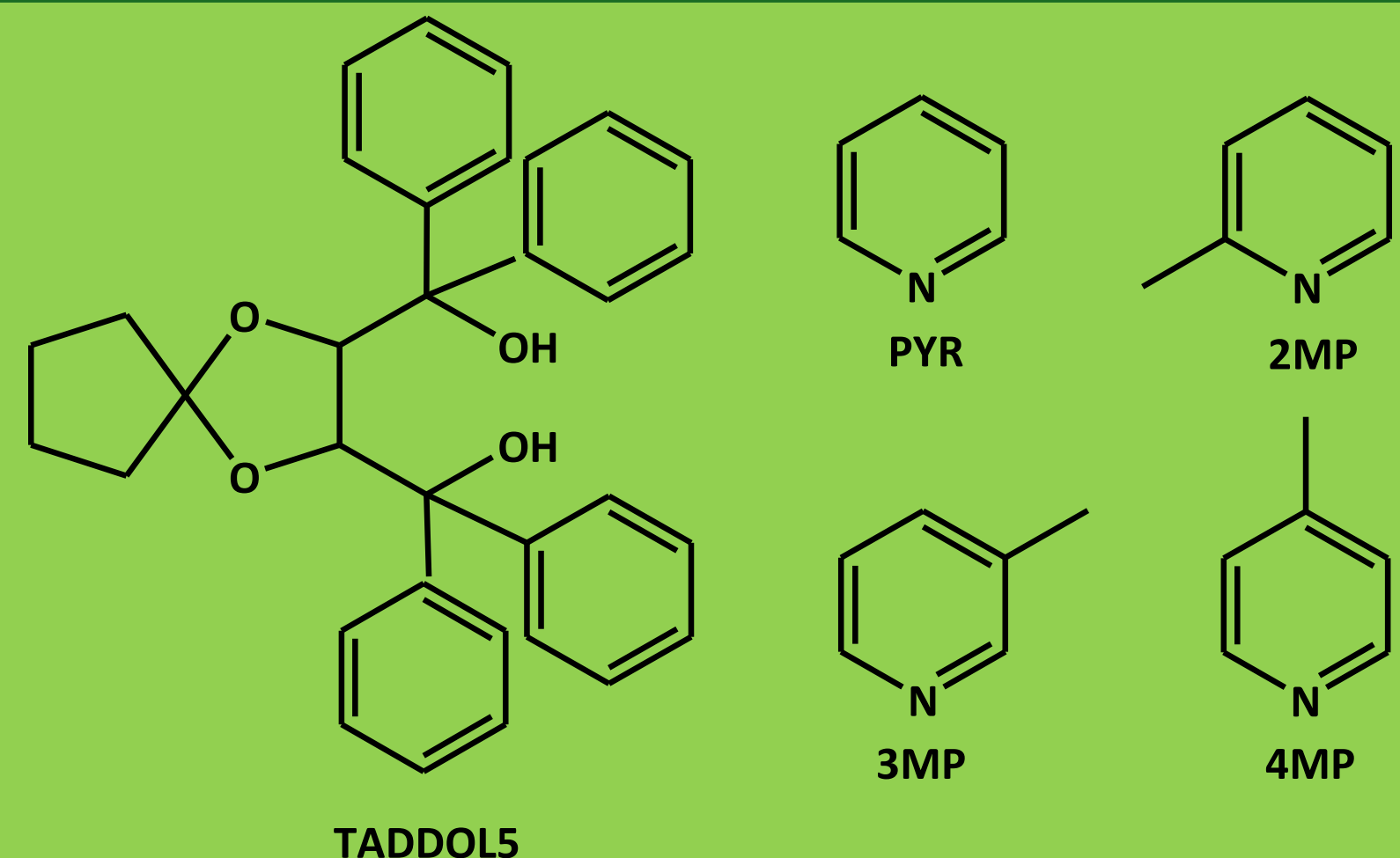
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Key factors of host-guest chemistry

Host-guest chemistry is a subset of supramolecular chemistry whereby a host binds to a guest to produce a host-guest complex.¹

These interactions are non-covalent and temporary in nature. Examples include $\pi\cdots\pi$ stacking interactions, $X-H\cdots\pi$ interactions and hydrogen bonding¹. An application of this type of host-guest chemistry is efficient separations of isomers; this method is green since the host itself is recyclable, complexation takes place at mild temperatures and the guest is released at low temperatures.¹

Applications



Scheme 1: The structures of TADDOL5 and the pyridine and methylpyridine guest solvents (PYR, 2MP, 3MP and 4MP).

- This is a new method of separation for isomers with narrow boiling ranges; fractional distillations are ineffective.²
- Pyridine (PYR) and the methylpyridines (2MP, 3MP and 4MP) are extremely important compounds in the chemical industry in their own right.^{3,4}
- Examples include:
 - PYR is a dipolar and aprotic solvent in synthetic procedures.^{3,4}
 - PYR and 3MP are precursors to insecticides.
 - PYR used in synthesis of the herbicides,⁵ and as an acid scavenger due to its basic character.⁶
 - The synthesis of 2-vinylpyridine requires 2MP.
 - 4MP is used in the production of the antituberculosis agent, isoniazid.

Experimental

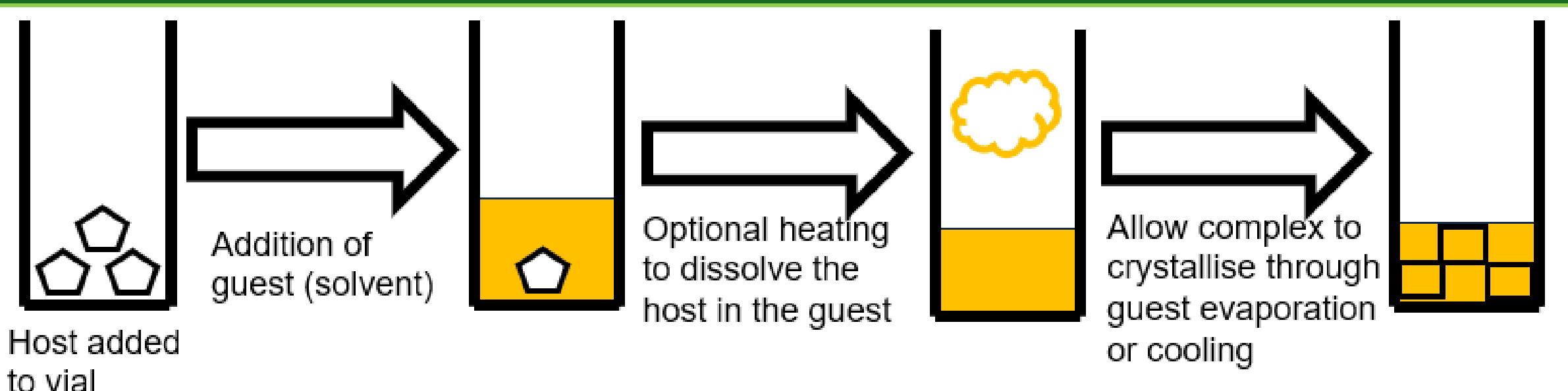
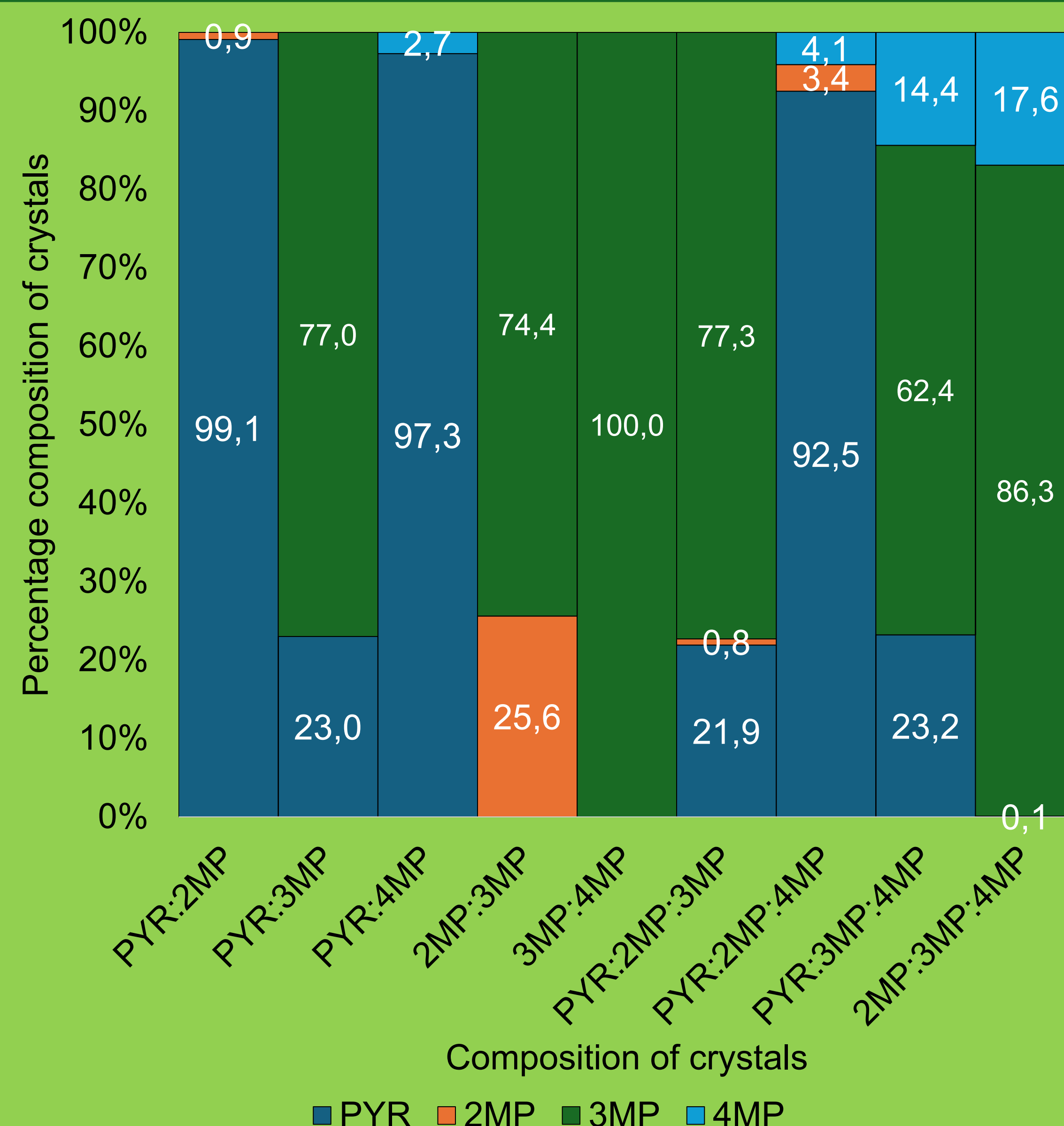


Figure 1: Method for complex formation.

For single solvent experiments, only one guest is used at a time.

In equimolar guest competition experiments, equal parts of the guests are added to make a total amount of 5 mmol, as illustrated in Figure 2. Several analysis techniques were employed including ¹H-NMR, TGA and SCXRD.

Single solvent and equimolar guest competition results



Guest	H:G ratio
PYR	1:1
2MP	1:1
3MP	1:1
4MP	1:1

Table 1: H:G ratios of complexes of TADDOL5 with the pyridyls.

It was determined that TADDOL5 formed 1:1 inclusion complexes with each member of the pyridyl series.

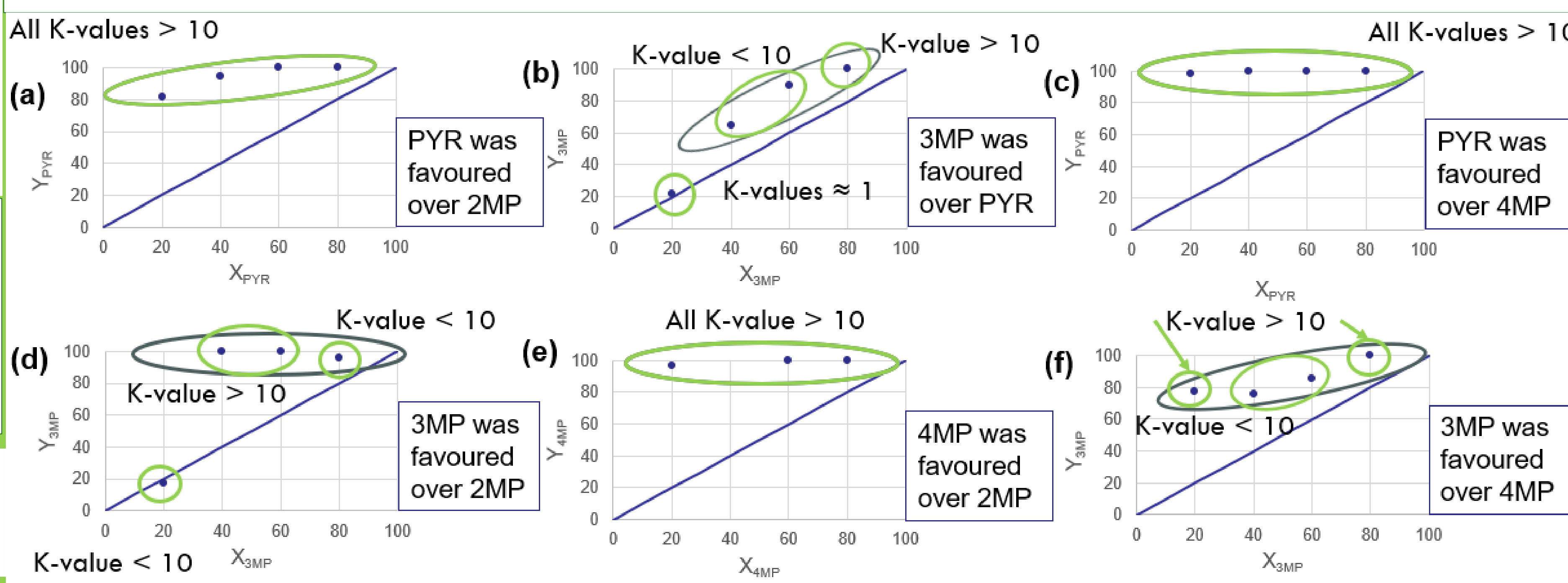
Figure 2: Guest ratios of mixed complexes from the equimolar crystallization experiments with TADDOL5.

The results of the equimolar guest competition experiments are summarised here. From this we can observe that 3MP was the most favoured guest. Pyridine was the second most favoured guest. The estimated standard deviation was calculated for each competition experiment and was sufficiently low.

Selectivity profiles

- The selectivity coefficient, K , is a measure of the selectivity of the host compound and may be calculated using⁷ $K_{G_A:G_B} = Y_{G_A}/Y_{G_B} \times X_{G_B}/X_{G_A}$ ($X_{G_A} + X_{G_B} = 1$).
- Low K values (normally around 9 or less) indicate low selectivities as reported by Nassimbeni and coworkers⁸.
- Values closer to 10 or more allude to the feasibility of employing the host compound for practicable binary guest solution separations.

Figure 3: Selectivity profiles for TADDOL5 in (a) PYR/2MP, (b) 3MP/PYR, (c) PYR/4MP, (d) 3MP/2MP, (e) 4MP/2MP and (f) 3MP/4MP binary mixtures where the straight diagonal lines represent a host compound that is not selective.



Single crystal X-ray diffractometry

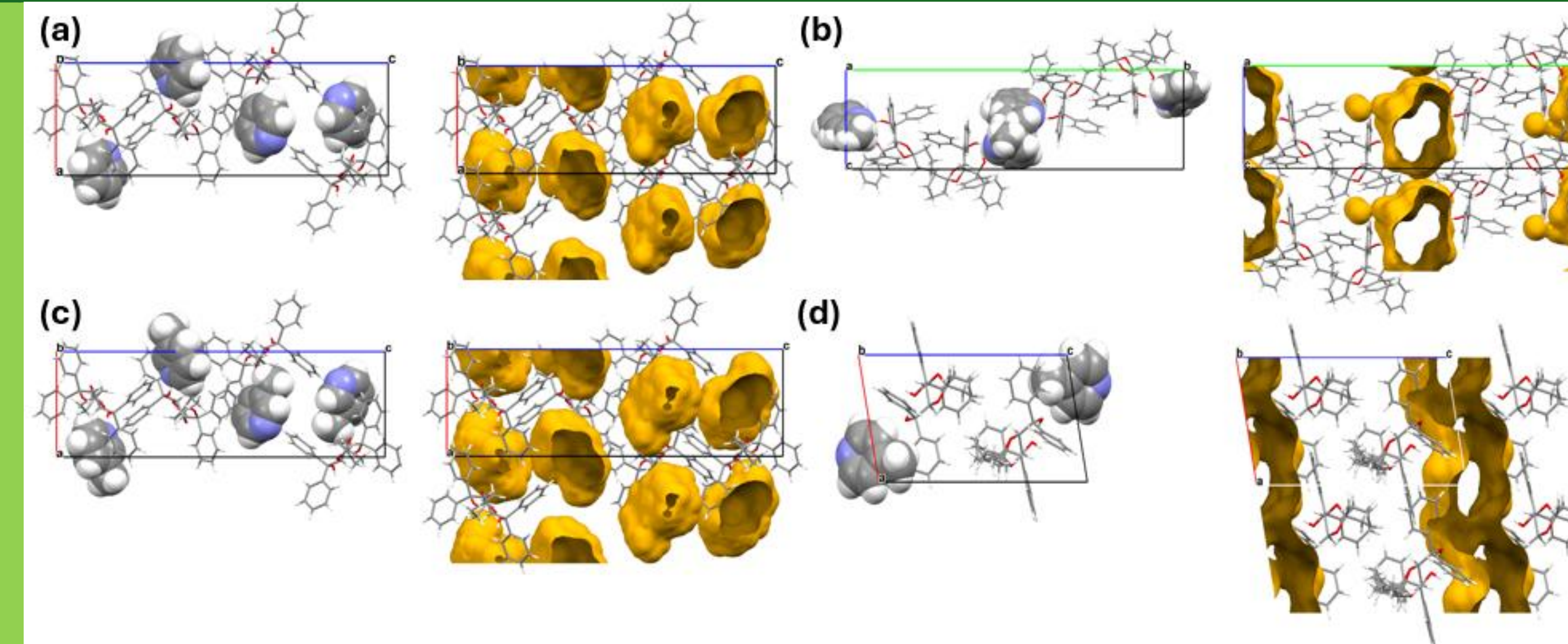
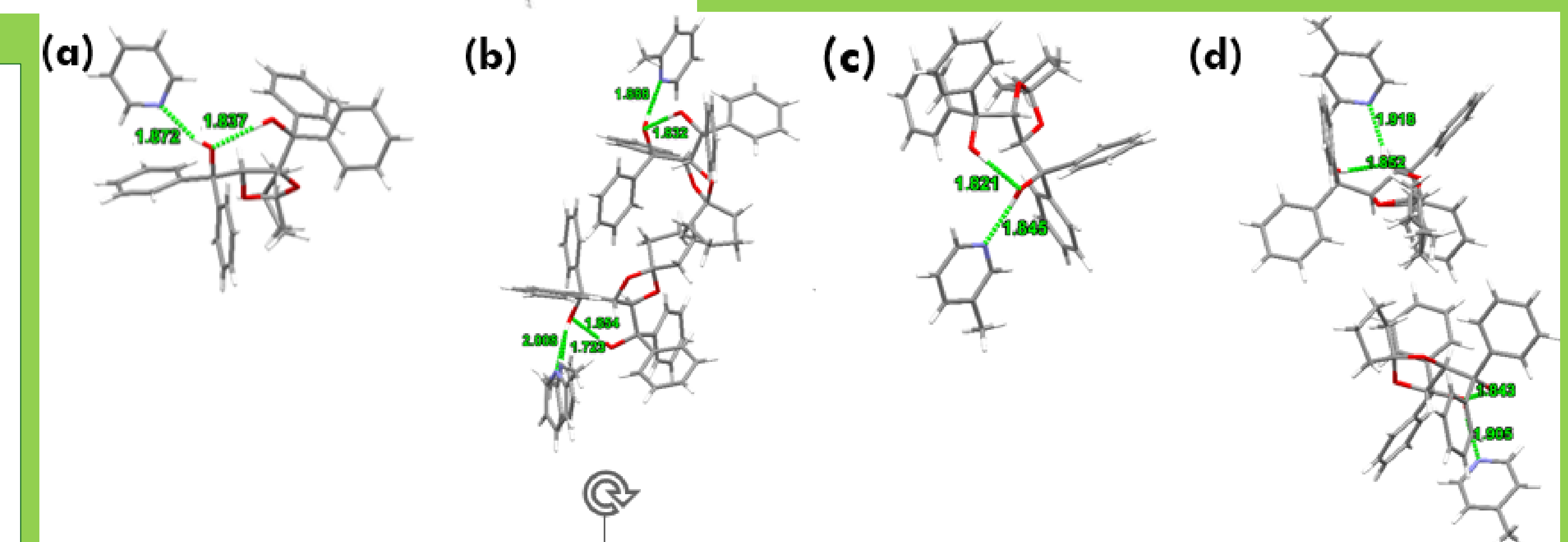


Figure 4: Unit cells (left) and voids (right) for (a) TADDOL5·PYR [010], (b) TADDOL5·2MP [100], (c) TADDOL5·3MP [010] and (d) TADDOL5·4MP [010]. The guest and host disorder are clear in (b) and (d), respectively.

TADDOL5·PYR and TADDOL5·3MP are isostructural due to their similar unit cell parameters. It is apparent that the preferred guest species of TADDOL5, PYR and 3MP, were accommodated in discrete cavities while those less favoured, 2MP and 4MP, were housed in endless channels.

Figure 5: The hydrogen bonds in (a) TADDOL5·PYR, (b) TADDOL5·2MP, (c) TADDOL5·3MP and (d) TADDOL5·4MP.

The shortest interaction was in the 3MP-containing complex followed by that in TADDOL5·PYR, in direct accordance with the selectivity behaviour of the host compound in the pyridyl guest mixtures.



Thermal analyses

Complex	T _{on} /°C	Mass loss expected/%	Mass loss measured/%
TADDOL5·PYR	73.4	13.8	16.1
TADDOL5·2MP	64.8	15.9	16.5
TADDOL5·3MP	79.4	15.9	16.1
TADDOL5·4MP	65.2	15.9	16.1

Table 3: Relevant thermoanalytical data for the complexes of TADDOL5 with the pyridine guest solvents.

T_{on}, a measure of the thermal stability of the complexes, is the guest release onset temperature. These values correlate with the observations of the guest competition experiments. 3MP and PYR were the preferred guest compounds as they formed the more thermally stable complexes compared with the less favoured 2MP and 4MP.

Conclusions

TADDOL5 was demonstrated to have host ability for PYR and the three MPs. TADDOL5 formed 1:1 H:G inclusion complexes with each one. Remarkable selectivities were observed for 3MP and PYR (in the absence of 3MP). The host affinity for 3MP may be due to the significantly shorter (host)O—H $\cdots$ N(guest) hydrogen bond followed by TADDOL5·PYR, indicating PYR is the second most preferred with 2MP and 4MP being the least preferred. Thermal analyses also confirmed the host affinity for 3MP and then PYR; 3MP formed a more stable complex with TADDOL5, followed by PYR; the 2MP- and 4MP-containing complexes were less stable. This investigation has demonstrated that very many of the pyridyl mixtures considered in this work may be separated by supramolecular chemistry strategies.

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